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THE MECHANISM OF THE PHOTOINDUCED HYDROGENATION OF 2,4-HEXADIENE CATALYZED BY CHROMIUM CARBONYL COMPLEXES

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Summary

The selectivity of the reaction with respect to the three isomers of 2,4-hexadiene depends on the precatalyst used and is discussed in the light of a general reaction scheme. The behaviour of this linear diene is compared with that of 1,3-cyclohexadiene.

Introduction

Preliminary results obtained with 1,3-cyclohexadiene, 2,4-hexadiene and 1,3-cyclooctadiene [1] suggested that two conditions must be satisfied in order to observe photoinduced hydrogenation catalyzed by chromium carbonyl complexes. Indeed, whereas the rate of hydrogenation of 1,3-cyclohexadiene was very fast compared with that of 2,4-hexadiene, 1,3-cyclooctadiene did not react at all under the same conditions. We thus assumed that the diene must not only be present in the *s-cis* conformation, but that the two ethylenic bonds must be coplanar. In agreement with this hypothesis *trans, trans*-2,4-hexadiene (*t, t*-Hex) was found to react faster than *cis, trans*-2,4-hexadiene (*c, t*-Hex) which was itself much more reactive than the *cis, cis* isomer in the presence of chromium hexacarbonyl*.

We have now investigated more thoroughly the behaviour of these derivatives by kinetic and spectrophotometric methods.

Results

(A). Hydrogenation of a mixture of 2,4-hexadiene isomers in the presence of chromium hexacarbonyl

When $Cr(CO)_6$ is irradiated in an n-pentane solution containing 55.5%

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* Preliminary results were obtained by A. Lentzen.

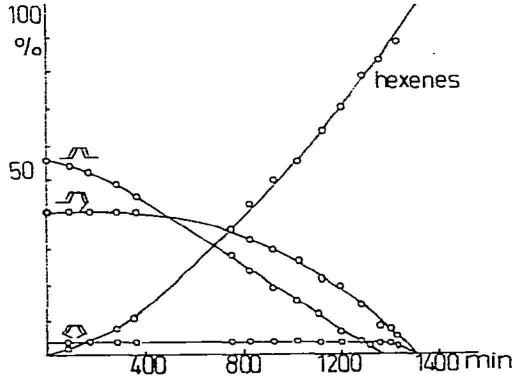


Fig. 1. 2,4-Hexadiene (100% = 6.6 X 10^{-2} *M*), and $Cr(CO)_6$ (8.6 X 10^{-4} *M*) in n-pentane. Hydrogen pressure 360 torr, λ 366 nm.

trans,trans-, 41% *cis,trans*- and 3.5% *cis,cis*-2,4-hexadiene, then *t,t*-Hex—$Cr(CO)_4$ [ν(CO) = 2035 m, 1962 m, 1942 s and 1927 s cm^{-1}] is formed selectively in the absence or presence of hydrogen. This complex is the only one formed from the chromium pentacarbonyl intermediate [ν(CO): 2075 w, 1957 s and 1948 m cm^{-1}] during the kinetic run depicted in Fig. 1. Hydrogenation yields two products: 96% *cis*-3-hexene and 4% of another olefin tentatively identified by infrared spectroscopy as *cis*-2-hexene. Figure 1 shows that, after a short induction period during which 2,4-hexadiene—$Cr(CO)_5$ and then *t,t*-Hex—$Cr(CO)_4$ are formed, selectivity towards the *trans,trans* isomer characterizes the hydrogenation, at least during the first hours of reaction.

Thorough analysis of the kinetics is impossible since the optical density of the solution changes during more than 6 hours irradiation, the time required to reach the point where the chromium tetracarbonyl complex absorbs all the light. Moreover, VPC analysis required the removal of aliquots of the solution in a stream of hydrogen, leading to uncontrolled amounts of free carbon monoxide in the reaction medium. The same optical bench as that used to study the norbornadiene reaction [2] was used in the present work and comparison of the reaction rates shows that 2,4-hexadiene is much less reactive than norbornadiene.

(B). Hydrogenation of a mixture of 2,4-hexadiene isomers in the presence of norbornadiene—$Cr(CO)_4$

So as to avoid the formation of pentacarbonyl complexes at the beginning of the run and an increase of free carbon monoxide during the run which might affect the kinetics, photoinduced hydrogenation was performed using norbornadiene—$Cr(CO)_4$ as precatalyst. Ultraviolet and visible as well as infrared spectra showed that while norbornadiene—$Cr(CO)_4$ was progressively hydrogenated (yielding nortricyclene and norbornene), *t,t*-Hex—$Cr(CO)_4$ was formed simultaneously. Two isosbestic points (λ 414 and 440 nm) observed in the visible spectrum, are accounted for by the transfer of a $Cr(CO)_4$ moiety from norbornadiene to the substrate. The products were the same as those reported in section (A). Figure 2 shows that selectivity towards the *trans,trans*

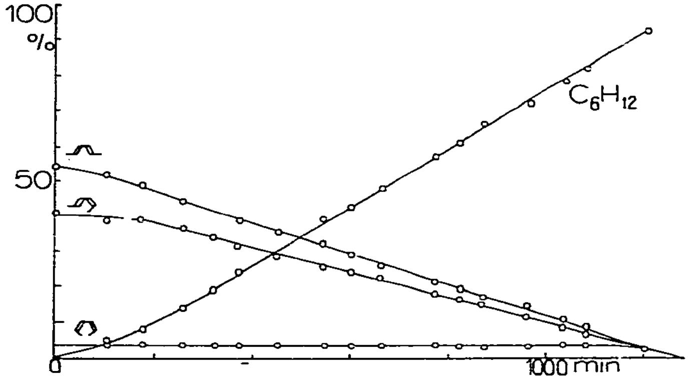


Fig. 2. 2,4-Hexadiene (100% = 6.6 × 10^{-2} *M*) and norbornadiene—$Cr(CO)_4$ (2.2 × 10^{-3} *M*) in n-pentane. Hydrogen pressure 360 torr, λ 366 nm.

isomer is no longer found and in this particular system (55.5% *trans,trans*, 41% *cis,trans* and 3.5% *cis,cis* isomers) comparison of the rate of conversion of the *trans,trans* and *cis,trans* isomers is consistent with a zero-order statistical reaction. This assumption is nevertheless erroneous since another experiment with a mixture of 37% *trans,trans*, 54% *cis,trans* and 9% *cis,cis* isomers, showed that the *trans,trans* isomer, although present in lower abundance, still reacted slightly faster than the *cis,trans* isomer.

When the sole chromium derivatives present in the solution are *t,t*-Hex—$Cr(CO)_4$ and unchanged norbornadiene—$Cr(CO)_4$, it seems that there is only a slight difference in reactivity of the various isomers.

In order to shed light on the part played by $Cr(CO)_6$ in the selectivity, a run similar to that reported in Fig. 2 was performed, this time in the presence of an additional amount of $Cr(CO)_6$ such that practically no light was absorbed by the latter.

Table 1 shows that the selectivity is increased although the photoinduced reaction involves only the diene—$Cr(CO)_4$ entities. $Cr(CO)_6$ mainly inhibits the hydrogenation of the *cis,trans* isomer, the rate of hydrogenation of the *trans, trans* isomer being only slightly affected.

(C). Separate hydrogenation of the cis,trans and trans,trans isomers in the presence of $Cr(CO)_6$

While the rate of reaction of pure *trans,trans* isomer in n-pentane solution is not very different from that of a mixture containing 12% *cis,trans* isomer, the

TABLE 1

HYDROGENATION OF 2,4-HEXADIENE CATALYZED BY NORBORNADIENE —$Cr(CO)_4$

	% Conversion	
	trans,trans	*cis,trans*
Norbornadiene—$Cr(CO)_4$ (1.2 × 10^{-3} *M*)	64.0	51.5
Norbornadiene—$Cr(CO)_4$ (1.2 × 10^{-3} *M*) + $Cr(CO)_6$ (1.8 × 10^{-3} *M*)	41.5	4.0

rate of conversion of pure *cis,trans*-2,4-hexadiene is much slower than its rate of reaction in the presence of *trans,trans* isomer. In other words, *cis,trans*-hexadiene does not strongly impede the hydrogenation of the *trans,trans* isomer, but the latter accelerates the conversion of the *cis,trans* isomer. Infrared spectroscopy shows that *c,t*-Hex—$Cr(CO)_4$ [ν(CO) 2032 m, 1953 m, 1932 s and 1924 s cm^{-1}]* is formed when no trace of *trans,trans* isomer is present to compete for complexation.

Hydrogenation of *t,t*-Hex yields 100% *cis*-3-hexene while *c,t*-Hex yields 89% *cis*-3-hexene and 11% *cis*-2-hexene.

(D). Deuteration of 2,4-hexadiene

Reaction conditions similar to those reported for hydrogenation yield 96% *cis*-2,5-dideutero-3-hexene and 4% *cis*-2-hexene. Because of the low concentration of the latter, the positions of deuteration could not be observed by NMR, a knowledge of which would have helped to decide between true 1,2-addition and a preliminary 1,5-hydrogen shift in *c,t*-Hex—$Cr(CO)_4$ followed by 1,4-addition of hydrogen to the resulting 1,3-hexadiene. Such a hydrogen shift has been previously postulated for the thermal hydrogenation of dienes [3].

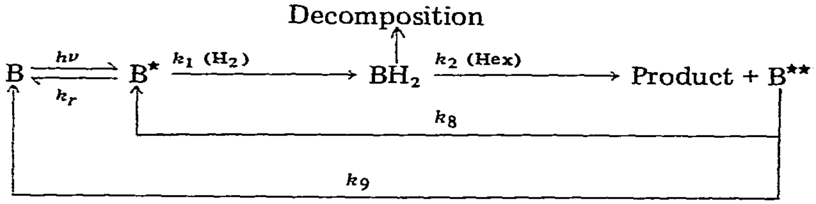
(E). Hydrogenation of 1,3-cyclohexadiene in the presence of norbornadiene—$Cr(CO)_4$

The reaction of a 7×10^{-2} *M* solution of cyclohexadiene is fast with 100% conversion in 84 minutes. [Norbornadiene (7×10^{-2} *M*) with norbornadiene—$Cr(CO)_4$ as catalyst requires 130 minutes under the same conditions]. The two isosbestic points at λ 397 and 442 nm observed in the visible spectrum are accounted for by the formation of 1,3-cyclohexadiene—$Cr(CO)_4$. This is confirmed by infrared analysis [ν(CO): 2040 m, 1973 m, 1952 s and 1932 s cm^{-1}].

Discussion

A reaction scheme has been proposed for the photoinduced hydrogenation of norbornadiene in the presence of norbornadiene—$Cr(CO)_4$ [2]. The relative slowness of the reaction of 2,4-hexadiene and the absence of first-order kinetics, prompt us to propose that, in this case, the mechanism does not involve the k_3 step leading to "free" $Cr(CO)_4$.

SCHEME 1



(B = 2,4-hexadiene—$Cr(CO)_4$; B* and B** are pentacoordinated hexadiene—$Cr(CO)_4$ labiles.)

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* Because of the presence of other complexes, e.g. the pentacarbonyl complex, the assignment of these bands to *c,t*-Hex—$Cr(CO)_4$ is tentative and less obvious than in the case of pure *t,t*-Hex.

We assume that the photoinduced opening of the diene chelate and the reaction of the pentacoordinated labile B^* with H_2 (k_1) are comparably efficient for 2,4-hexadiene and for norbornadiene. Moreover, the thermal chelation of B^* and B^{**} (k_r and k_9) giving B, must be less easy for linear than for dienes. The k_2 step comprising hydrogen transfer from Cr to the hydrocarbon moiety must be strongly dependent on the nature of the latter.

We propose that in the intermediate BH_2 the diene must adopt an *s-cis* planar conformation to allow addition of hydrogen; such a conformation being quite natural for 1,3-cyclohexadiene and norbornadiene, but less readily attained by the linear 2,4-hexadienes and in particular by the *cis,cis* and *cis,trans* isomers. The absence of coplanarity of the two ethylenic bonds in 1,3-cyclooctadiene would be responsible for its complete inertness. Interestingly, although irradiation of $Cr(CO)_6$ in the presence of a conjugated diene yields a diene—$Cr(CO)_4$ complex, 1,3-cyclooctadiene forms only a pentacarbonyl complex [ν(CO): 2070 w, 1955 s and 1948 m cm^{-1}].

The sequence of reactivity being thus explained, Scheme 1 should account for the acceleration of the hydrogenation of *c,t*-Hex in the presence of *trans, trans* isomer. Indeed we have seen that light is absorbed by *t,t*-Hex—$Cr(CO)_4$, leading to the formation of *trans,trans* BH_2, which will then decompose in the presence of either *trans,trans* hexadiene or *cis,trans*-hexadiene; in the latter case, *cis,trans*-B^{**} will be formed in a fairly efficient way, allowing the *cis,trans* isomer to be involved in the catalytic cycle. The reasons why formation of pentacoordinated *cis,trans*-B^* by direct irradiation of *c,t*-Hex—$Cr(CO)_4$ is less efficient, than this process, are not apparent to us. Infrared spectroscopy shows that when $Cr(CO)_6$ is photolyzed in the presence of *cis,trans*-hexadiene, as usual the chromium pentacarbonyl complex is formed initially (but then it persists in solution together with other unidentified complexes) and a clean pattern of the four bands assigned to *c,t*-Hex—$Cr(CO)_4$ is never observed.

Better resolution of the spectrum would be necessary to elucidate the precise nature of the changes in solution and to allow a better understanding of the relative inability of *c,t*-Hex—$Cr(CO)_4$ to induce photocatalyzed hydrogenation.

Labile BH_2 complexes do not accumulate and will react with any scavenger present in solution. $Cr(CO)_6$ and free carbon monoxide may well both be efficient in such a process and this would account for their role in selectivity: a higher concentration of labile complexes able to react with $Cr(CO)_6$ corresponds to a smaller value of k_2. We do not know the nature of such reactions but in support of this hypothesis, no decrease in hydrogenation rate was observed with norbornadiene (high k_2 value assumed) when $Cr(CO)_6$ was added to a comparison solution containing norbornadiene—$Cr(CO)_4$ as catalyst.

When $Cr(CO)_6$ is irradiated in the presence of *c,t*-Hex but in the absence of H_2, traces of *t,t*-Hex—$Cr(CO)_4$ are formed. *Cis,trans* isomerization during the hydrogenation runs is probably negligible in view of the small quantum yields observed by Gray and co-workers [4], in the presence of $W(CO)_6$, compared with the hydrogenation quantum yield (approximately 0.3 for *trans,trans* isomer): $W(CO)_6$ and $Mo(CO)_6$ are less effective as hydrogenation photocatalysts than $Cr(CO)_6$ and both give photo-assisted isomerization [5].

Experimental

2,4-Hexadiene [6] was purified and the various isomers were separated on a Ucon-oil column (5 m length). Experimental conditions were identical to those described previously [2].

Attempts to isolate 2,4-hexadiene—Cr(CO)$_4$ and 1,3-cyclohexadiene—Cr(CO)$_4$ were unsuccessful; these complexes are quite stable in solution (n-pentane) at room temperature in the presence of free diene, but on evaporation of the latter under high vacuum, they decompose. Probably thermal opening of the chelate and equilibrium with (diene)$_2$ Cr(CO)$_4$ occur in solution, causing only apparent stability.

Acknowledgements

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