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CATALYTIC HYDROGENATION OF HETEROCYCLIC COMPOUNDS.(II)[1]. BOND ISOMERIZATION AND HYPERSTABILITY

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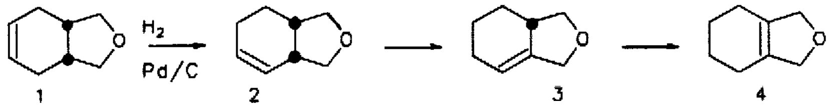
ABSTRACT: Bond isomerization is common during catalytic hydrogenation reactions. Recent studies have focused on examining alkenes that reduce only with great difficulty. The concept of hyperstability has been used to account for the observed non-reactivity. In this work we examine both problems and suggest an explanation to account for hyperstability.

Bond isomerization during heterogeneous catalytic hydrogenation is often-observed[2], and has been long incorporated into the classic mechanism of Horuiti and Polanyi[3]. As a consequence of our continuing interest in the effects of the ether functional group on catalytic hydrogenation of heterocyclic compounds[4], we noticed rapid isomerization of 1 to 4 during the reduction process (Scheme 1). Isomers 2[4] and 4 were identified by unambiguous syntheses; 3 was characterized by ^{1}H-NMR.



Scheme 1. Bond Isomerization During Catalytic Hydrogenation

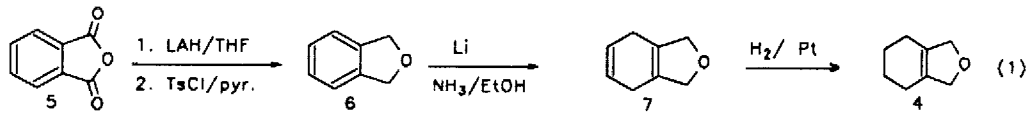
Because olefin isomerization during heterogeneous catalytic hydrogenation is considered to be an equilibrium process, we examined by calculational methods the thermodynamic stabilities of the olefinic isomers. The MM2-generated strain energies (SE), the derived olefinic strain energies (OS), and heats of formation (H_f) are reported in Table 1. The OS is obtained by subtracting the total strain energy of the most stable conformer of the parent hydrocarbon from that of the olefin, also in its most stable conformation.[5]

Table 1. MM2-Generated Energies (Kcal/mole)

Olefin	SE	OS	H_f
1	9.98	0.83	-28.86
2	8.30	0.15	-30.54
3	6.94	-1.21	-33.50
4	5.04	-3.11	-37.00
Saturated	8.15	-----	-58.80

These data show that the alkene stability, as reflected by lower values for OS, increases as the alkene isomerizes, becoming more substituted - not an unexpected observation. However, these results parallel trends observed by Schleyer for a class of compounds he has defined as "hyperstable" olefins - medium-sized polycyclic ring systems with bridgehead double bonds and possessing negative OS energies[6]. These olefins also have low heat of hydrogenation; and some are resistant to hydrogenation.[7] The surprising stability of these compounds is in sharp contrast to the stability found in smaller bridgehead olefins.

Although highly substituted alkenes have long been thought to resist reduction because of "steric effects", this exciting approach suggests that readily-obtained MM2 data can be used to predict resistance to hydrogenation. Indeed, we used the relative reactivities to hydrogenation in our preparation of **4** (Equation 1).



Is there a fundamental rationale for hyperstability? Unfortunately, as Schleyer has pointed out for molecules he investigated, molecular orbital calculations on complex molecules require a large allocation of computer time. However, molecules used in our study are relatively simple. MNDO calculations on 1-4 also reveal in the heats of formation a large thermodynamic driving force to bond isomerization (TABLE 2), although poor (but not unexpected) agreement with MM2 values is observed.

TABLE 2. MNDO Calculated Heats of Formation

Olefin	Hf (Kcal/mol)
1	-42.90
2	-44.47
3	-47.36
4	-50.43

Additional insight was obtained from the calculated HOMO pi-bond orders (Table 3) and HOMO contour plots (Figure 1). From the data in Table 3 we see a 20% decrease in the HOMO pi-bond orders between 1 and 4. We see the origins of this in Figure 2 where we see increasing electron delocalization in 1-4.

Table 3. HOMO P_z Atomic Orbital Coefficients and HOMO Bond Order.

Olefin	Cp_{zi}	Cp_{zj}	π BO
1	.65062	.65060	.8466
2	.64978	.64484	.8380
3	.61811	.62237	.7694
4	.58179	.58200	.6772

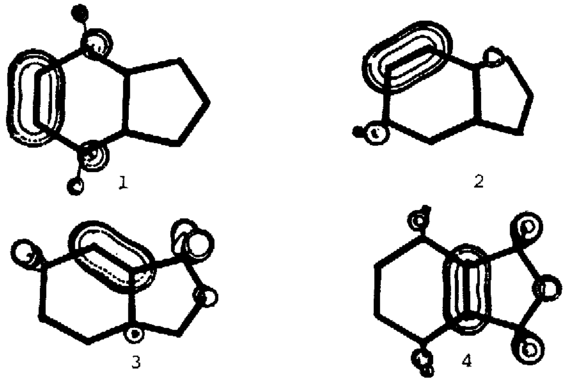


Figure 1. ***HOMO*** **Contour Plots**

These data show a direct correlation between decreasing OS energies, ie, "hyperstability" and decreasing **HOMO** pi-bond order. A 20% decrease in the **HOMO** pi-bond order is found in this series. This suggests that the fundamental origin of hyperstability may be found in the classical idea of hyperconjugation. Additional studies are in progress to test this concept.

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