formamide (83%)[8] were recovered.

^{1}H NMR Measurements. Known amounts of a stock solution (2 M in $CDCl_3$) of the compounds under examination (namely DOA, DDA, and $EtOCON_3$) were added to 0.5 mL of $CDCl_3$ in a 5-mm NMR tube. The spectrum of the resulting solution at a concentration ranging between 0.6 and 0.001 M at 35 °C was recorded in the FT mode with 40° flip angle, 16K words, and 0.12 Hz of digital resolution, the number of scans depending on the concentration of the solution. Chemical shifts are referenced to internal Me_4Si.

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Registry No. (*E*)-**1a**, 107244-94-0; (*Z*)-**1a**, 107244-95-1; (*E*)-**1b**, 107244-97-3; (*Z*)-**1b**, 107244-96-2; DOA, 7378-99-6; DDA, 112-18-5; DOAP, 107244-98-4; $EtOCON_3$, 817-87-8; EtOCON, 2655-26-7; $H_3C(CH_2)_7N(CHO)CH_3$, 36600-01-8; $H_3C(CH_2)_{10}N(CHO)CH_3$, 76058-02-1.

Heterogeneous Catalysis in Organic Chemistry. 7.[1] Stereochemistry of the Hydrogenation of 1,3,5-Trimethylcyclohexene

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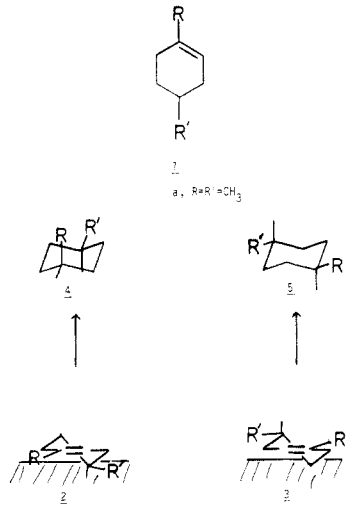
The product stereochemistry observed on catalytic hydrogenation of alkyl-substituted cycloalkenes can be related to the relative ease with which the two faces of the double bond can be adsorbed on the catalyst surface. With 1,4-dialkylcyclohexenes **1**, these two modes of adsorption can be represented as in **2** and **3**. The product obtained



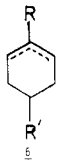
by hydrogen transfer from the catalyst surface to **2** is the *cis*-dialkylcyclohexane **4**. The trans product **5**, is obtained from the alternate adsorption mode, **3**. Published data[2,3] indicates that with **1a** there is an almost equal degree of hindrance between **2** and **3** with 57% of the cis product obtained on hydrogenation over PtO_2 in HOAc at ambient conditions (Table I). As the homoallylic substituent, R', increases in size from Et → *i*-Pr → *t*-Bu the amount of **4** obtained decreases in order from 48% → 43% → 37%[4] so the size of this substituent presents more steric hindrance in **2** than in **3**. Changing the size of the vinyl substituent, R, from Me → Et → *i*-Pr with R' as a Me gave no change in the amount of **4** obtained[4] so the vinyl substituent has no significant steric influence on the reaction. Similar steric effects are also observed with a Rh/C catalyst.[2]

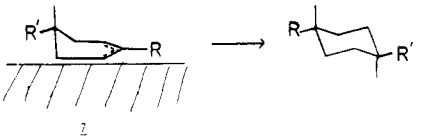
Table I. Percent Cis Product Formation on Hydrogenation of Methyl-Substituted Cyclohexenes

	substrate			
catalyst	**8**[a]	**9**[a]	**1a**[a]	**14**[b]
Pt	72 (74)[c]	59	57 (61)[d]	60
Rh	74	49	57 (57)[d]	54
Pd	80	80	27 (28)[d]	73

[a] Reference 3. [b] This work. [c] Reference 4. [d] Reference 2.

With Pd catalysts, though, all 1,4-dialkylcyclohexenes are reported to give only 20–30% of the cis product regardless of the substituents.[2,5,6] This is apparently the result of the presence on the catalyst surface[6] of the π-allyl intermediate **6**, which is most favorably adsorbed in the trans mode, **7**, with the size of the R' group only of secondary importance.





The hydrogenation of 1,3-dialkylcyclohexenes presents a different situation since two trisubstituted double bond isomers such as **8** and **9** are possible with this system. As the data in Table I show, hydrogenation of **8** over either Pt or Rh catalysts gives about 75% of the cis product **12**. Hydrogenation of **9** over Pt gives about 60% of **12**, while over Rh almost 50% of **12** is obtained.[3] The adsorption modes of **8** can be illustrated by **10** and **11** leading to the cis, **12**, and trans, **13**, products respectively. From the product distribution obtained it is apparent that the allylic substituent in the ψ axial conformation as in **11** exerts a considerable steric influence on the way **8** is adsorbed on the catalyst.

The adsorbtion modes for **9** are essentially those depicted as **2** and **3** but having the R group on the other vinyl carbon so in this system, as with **1a**, product stereochemistry is expected to be controlled by the homoallylic substituent. It is not surprising then that both **9** and **1a** give the same amount of cis product on hydrogenation over Pt (Table I). The data for the Rh-catalyzed hydrogenation of **9** appears to be anomolous. From the difference in

(1) For Part 6, see: Augustine, R. L.; Thompson, M. M.; Doran, M. A. *J. Org. Chem.*, in press.
(2) Hussey, A. S.; Schenack, T. A.; Baker, R. H. *J. Org. Chem.* **1968**, *33*, 3258.
(3) Mitsui, S.; Imaizumi, S.; Nanbu, A.; Senda, Y. *J. Catal.* **1975**, *36*, 333.
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(5) Sauvage, J. f.; Baker, R. H.; Hussey, A. S. *J. Am. Chem. Soc.* **1961**,*83*, 3877.
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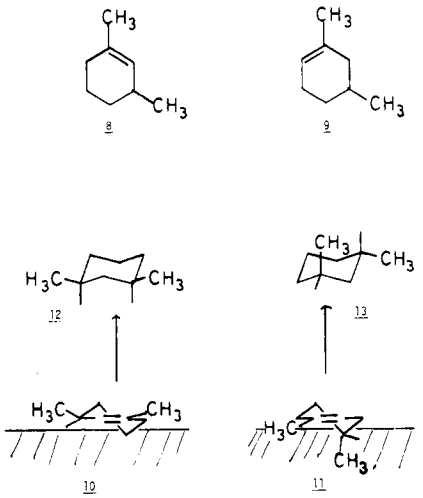
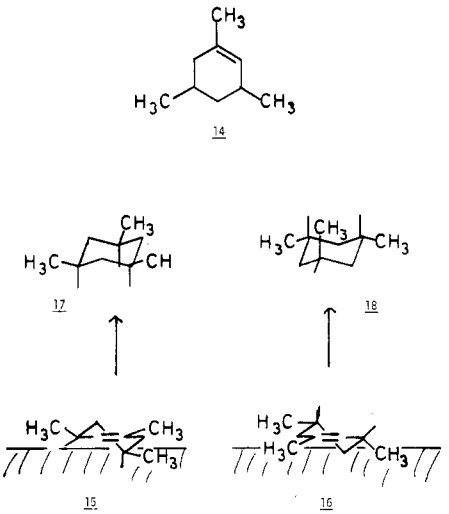


product compositions obtained from 8 and 9 it appears that double bond isomerization is not occurring during these hydrogenations, but this cannot be completely ruled out on the basis of the available data. Further, it would seem that a substituent in the allylic position as in **10** and **11** exerts more steric control over the hydrogenation than does one in the homoallylic position as in **2** and **3**.

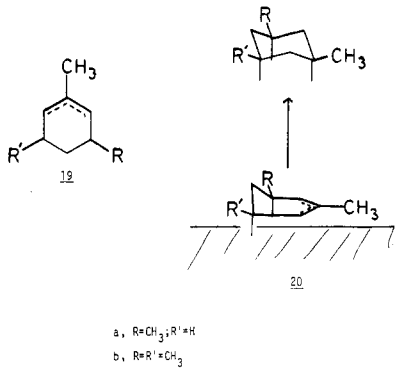
To determine whether this was the case or not the catalytic hydrogenation of 1,3,5-trimethylcyclohexene (**14**) was run over Pt, Rh, and Pd catalysts in ethanol under ambient conditions with the results listed in Table I. This molecule was chosen for two reasons. In the first place all double bond positions are equivalent so if double bond isomerization does take place it will have no influence on the outcome of the reaction. Second, as shown by the



adsorption modes **15** and **16** both allylic and homoallylic substituents are present so one should be able to determine which is the more critical in determining product stereochemistry.

From the data in Table I it can be seen that hydrogenation of **14** over Pt and Rh gives essentially the same amount of cis product as is obtained on hydrogenation of **1a** and **9**. This indicates that the homoallylic methyl group as in **2** and **3** is more influential in determining product stereochemistry than is the allylic methyl. Further, the close correspondence of results between **14** and **9** also indicates that there is little, if any, double bond isomerization taking place on hydrogenation of **9**.

The hydrogenations of **8**, **9**, and **14** over Pd all give predominantly the cis product **12** from **8** and **9** and **17** from **14**. This is not surprising since these three alkenes would form the π-allyl **19**, which would have its primary adsorption mode as depicted in **20**.



a, R=CH_3; R'=H
b, R=R'=CH_3

Experimental Section

1,3,5-Trimethylcyclohexene (**14**) was prepared by the addition of *cis*-3,5-dimethylcyclohexanone to a solution of methylmagnesium iodide and the product alcohol dehydrated by using standard procedures:[7] bp 141–143 °C (lit. 142.5–143.5 °C).[8]

The hydrogenations were run with 0.5 mL of **14** in 20 mL of purified ethanol over 50 mg of either 5% Pt/C, 5% Rh/C, or 5% Pd/C catalyst under ambient conditions in a sloping manifold hydrogenator using previously published procedures.[6] The catalysts used were the same as those used in previous studies.[6,7] After completion of the hydrogenation a sample of the product mixture was analyzed by gas chromatography through a 45 ft × $^1/_4$ in. column of 10% DEGS on Chromosorb P at 130 °C and a flow rate of 45 mL He/min. The products were identified by comparison of their retention times with authentic materials prepared by the hydrogenation of 1,3,5-trimethylbenzene under reported conditions.[9]

Acknowledgment. This work was supported, in part, by Grant DE-FG 0284ER45120 from the U.S. Department of Energy, Office of Basic Energy Sciences.

Registry No. **14**, 3643-64-9; Pt, 7440-06-4; Rh, 7440-16-6; Pd, 7440-05-3.

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Synthesis of Novel 8-Arylimidazo[1,2-*a*]pyridines and 8-Arylimidazo[1,5-*a*]pyridines

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As part of a program intended to study novel heterocycles related to purine,[1] we required synthetic methodology that could be used to conveniently prepare 8-arylimidazo[1,2-*a*]pyridines and -imidazo[1,5-*a*]pyridines. In addition, we were interested in methodology that could be general in its scope such that several derivatives could be obtained for use in structure–biological activity studies.

While several methods for preparing imidazo[1,2-*a*]-pyridines (**1**) have been reported,[2,3] the most common method remains that first reported by Tschitschibabin,[4]

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(2) Mosby, W. L. *Heterocyclic Systems with Bridgehead Nitrogen Atoms*; Interscience: New York, 1961; Vol. XV, Part 1.
(3) Lumma, W. C., Jr.; Springer, J. P. *J. Org. Chem.* **1981**, *46*, 3735.

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