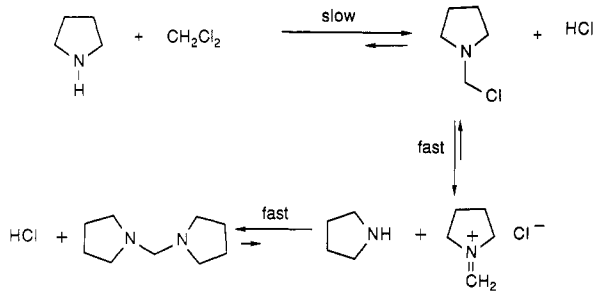
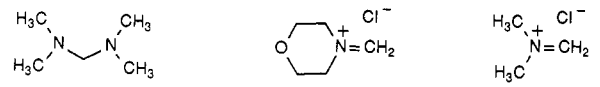
Scheme I



methanaminium chloride (6) and 20% 4-methylenemorpholinium chloride.



4 5 6

These data provide evidence that 1-methylenepyrrolidinium chloride could have been produced in the ^{13}C NMR experiments described above, but remained unobserved due to a change in the chemical shift. However, they do indicate that **2** is not the major species in solution at the end of the reaction.

Experiments run by addition of excess pyrrolidine to pure 1-methylenepyrrolidinium chloride (**2**) showed immediate loss of the resonance at 8.81 ppm with formation of a broad singlet at 3.2 ppm in the ^1H NMR. Upon quenching the reaction with $NaOD/D_2O$, this resonance remained. These data indicate that the formation of aminal from 1-methylenepyrrolidinium chloride and pyrrolidine is very rapid.

A mechanism which accounts for the kinetics observed by Songstad[2] as well as for the products observed in these and other studies is shown in Scheme I. If the condensation of methylene chloride with a secondary amine is the rate-determining step in the sequence leading to aminal, pseudo-first-order kinetics will be observed for this reaction. Whether or not the absolute values of the rate constants for the reactions of amine with methylene chloride determined by Nevstad and Songstad turn out to be correct, the values may serve as an indicator of relative reactivity of the amines.

From our study we conclude (1) that pyrrolidine rapidly reacts with methylene chloride solvent molecules at room temperature, (2) that in the absence of additional base, the major products in this reaction are 1,1′-methylenebis(pyrrolidine) and pyrrolidinium hydrochloride, and (3) that 1-methylenepyrrolidinium chloride, a presumed intermediate in the formation of the aminal, reacts so rapidly with pyrrolidine and/or aminal that its presence as a distinct species can not be established. These conclusions are what is expected based upon literature precedent.[1,9,13,14]

Methylene chloride has been reported[14] to be one of the best solvents for the reaction of tertiary amines with alkyl halides. It should not be surprising, then, that reactions of primary, secondary, and tertiary amines with this solvent are common. Although quantitative work in this area is difficult due to the frequent formation of inhomogeneous reaction mixtures, quantitative,[2] and qualitative[1] studies have been reported. Tertiary amines frequently form quaternary chloromethylammonium salts with methylene chloride. Secondary amines can react rapidly to yield mixtures of amine hydrochloride and aminal or in the presence of additional base to give high yields of pure aminal. Aminal formation from secondary amines is apparently occurring through the intermediacy of the corresponding methyleneiminium chloride which reacts rapidly with another molecule of the starting amine.

Since methylene chloride is frequently used in extractions and those solutions are, on occasion, allowed to stand at room temperature for extended periods, reaction yields can be adversely affected through formation of undesired byproducts. Care should be exercised when this solvent is used with amines to avoid conditions which can favor byproduct formation.

(14) Abraham, M. H.; Grellier, P.L. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1735.

Experimental Section

AR grade methylene chloride was used without additional purification. The solvent was shown not to contain bromochloromethane by mass spectrometry. ^1H NMR spectra were obtained on a Varian EM390 spectrometer. ^{13}C NMR spectra were obtained on a JEOL JNM-FX60Q (60 MHz) instrument. As noted above, $CDCl_3$ or CH_2Cl_2 was used as the solvent in all NMR studies. Tetramethylsilane was used as internal reference for ^1H NMR spectra. The internal reference for ^{13}C NMR spectra was $CDCl_3$ or benzene-d_6.

1,1′-Methylenebis(pyrrolidine) (1) was prepared by stirring pyrrolidine (7.1 g, 0.1 mol) with methylene chloride (60 mL) in the presence of 30% aqueous sodium hydroxide (10 mL) for 18 h at room temperature.[1] The product was purified by distillation under reduced pressure.

1-Methylenepyrrolidinium chloride (2) was prepared by the method of Böhme[11] in 94% yield from 1,1′-methylenebis(pyrrolidine). The compound is extremely hygroscopic and gradually decomposes to formaldehyde and pyrrolidine hydrochloride when exposed to humid air.

Acknowledgment. We acknowledge the work done by Susan Campbell and Martin Mutter in obtaining ^{13}C NMR spectra and thank Dr. Vasken Paragamian, Martin Mutter, and Dr. Ruth Inners for helpful discussions.

Registry No. 1, 7309-47-9; 2, 52853-03-9; pyrrolidine, 123-75-1; methylene chloride, 75-09-2.

Tertiary Amine Microaggregate Control of (Ethoxycarbonyl)nitrene Regioselectivity[1]

Riccardo Bertolaccini, M. Antonietta Loreto,* Lucio Pellacani,* and Paolo A. Tardella*

Dipartimento di Chimica, Università La Sapienza, I-00185 Roma, Italy

Giorgio Cerichelli*

Centro CNR di Studio sui Meccanismi di Reazione, Dipartimento di Chimica, Università La Sapienza, I-00185 Roma, Italy

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It is well-known that nitrenes are interesting reagents for the introduction of a nitrogen functionality in many organic compounds.[2] Despite this fact, nitrenes are rarely used in synthetic chemistry owing to their poor selectivity.

Our recent results[3] encouraged us to try a new approach to induce selectivity in reactions involving nitrenes. There

(1) A preliminary account has been presented at the Fourth European Symposium on Organic Chemistry (ESOC IV), Aix-en-Provence, France, Sept 2–6, 1985; Abstract PB-14.

(2) Scriven, E. F. V., Ed. *Azides and Nitrenes, Reactivity and Utility*; Academic: Orlando, FL, 1984.

(3) (a) Fioravanti, S.; Loreto, M. A.; Pellacani, L.; Tardella, P. A. *J. Org. Chem.* **1985**, *50*, 5365. (b) Bertolaccini, R.; Cerichelli, G.; Loreto, M. A.; Pellacani, L.; Tardella, P. A. *Gazz. Chim. Ital.* **1986**, *116*, 587.

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Table I. Isolated Yields of Formamidines 1 from Photolysis of $EtOCON_3$ in the Presence of DOAP, DOA, and DDA

substrate (concn, M)	solvent	yield of 1, %	substrate (concn, M)	solvent	yield of 1, %
DOAP (1)	$CHCl_3$	15	DOA (0.04)	$CHCl_3$	ND[a]
DOAP (0.1)	$CHCl_3$	ND[a]	DOA (1)	CH_2Cl_2	36
			DOA (0.04)	CH_2Cl_2	31
DOAP (0.04)	$CHCl_3$	ND[a]	DDA (1)	$CHCl_3$	24
			DDA (0.1)	$CHCl_3$	ND[a]
DOAP (1)	CH_2Cl_2	45	DDA (0.04)	$CHCl_3$	ND[a]
DOAP (0.04)	CH_2Cl_2	30	DDA (1)	CH_2Cl_2	35
			DDA (0.1)	CH_2Cl_2	31
DOA (1)	$CHCl_3$	27	DDA (0.04)	CH_2Cl_2	24
DOA (0.1)	$CHCl_3$	ND[a]			

[a] ND = not detected.

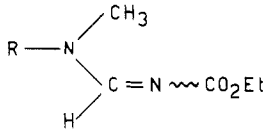
are examples in literature[4] showing that it is possible to obtain a good to high control of regioselectivity in reactions using micellar systems.

To the best of our knowledge, only one paper exists[5] describing the reaction of a nitrene in the presence of cationic micelles in water to functionalize aromatic or aliphatic hydrocarbons with the usual selectivity. We decided to investigate the photolysis of ethyl azidoformate ($EtOCON_3$) in the presence of long-chain ammonium salts that are known to form reverse micelles in nonpolar solvents[6] and to study this reaction under the same conditions with the corresponding amines that were not supposed to aggregate under such conditions.

Results and Discussion

We tested *N,N*-dimethyloctylammonium propionate (DOAP), *N,N*-dimethyloctylamine (DOA), and *N,N*-dimethyldodecylamine (DDA) in chloroform or dichloromethane in concentrations ranging from 0.04 to 1.0 M. The molar ratio between ethyl azidoformate to substrate was always maintained equal to 1.5.

The photolysis of $EtOCON_3$ in the presence of DOAP (1 M), carried out in $CHCl_3$, showed as the main product (*Z,E*)-N^2-(ethoxycarbonyl)-N^1-methyl-N^1-octylformamidine (**1a**) (see Table I). Neither products of func-



1

a, R = n-C_8H_{17}

b, R = n-$C_{12}H_{25}$

tionalization of the octyl chain nor the products of attack on the propionate ion have been detected. No trace of any product was detected at DOAP concentration of 0.1 or 0.04 M. Ethyl urethane was always present as byproduct.

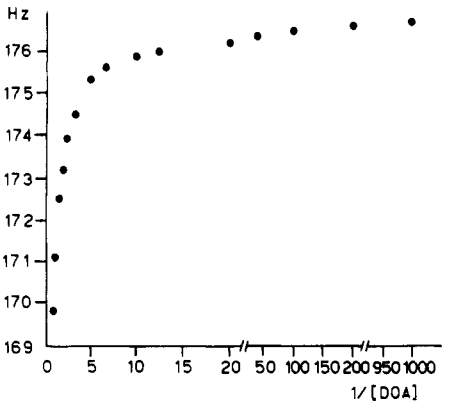


Figure 1. Chemical shift of the NCH_3 protons of DOA vs. 1/[DOA] in $CDCl_3$ at 35 °C.

Again the formamidine **1a** (*E* + *Z* mixture) was obtained in comparable yields when the photolyses were carried out in CH_2Cl_2 using the two limiting salt concentrations (1 and 0.04 M) utilized in $CHCl_3$.

The free base *N,N*-dimethyloctylamine (DOA) gave quite similar results, when submitted to the same reaction conditions. DDA behaved in an analogous way, the same kind of solvent effect was noted, and (*Z,E*)-N^2-(ethoxycarbonyl)-N^1-methyl-N^1-dodecylformamidine (**1b**) was the product (see Table I).

Both geometric isomers of 1 have been observed by ^1H and ^{13}C NMR: in fact, all the carbons adjacent to both nitrogen atoms showed double signals; the same was true for the relative attached protons (isomer ratio 60:40). The mixtures equilibrate spontaneously to give only the minor isomers, probably the *E* isomers.[7] The hydrolysis of formamidines 1 to the corresponding formamides and ethyl urethane was easily carried out by treatment with 10% acetic acid in water–dioxane (1:2 v/v) at 20 °C for 1 h.

In this manner it is possible to perform a selective oxidation of an *N,N*-dimethylalkylamine,[8] the key step being a clean insertion of (ethoxycarbonyl)nitrene (EtOCON) into C–H bonds of the methyl group; the insertion product was not detected, and we suppose a hydrogen abstraction by nitrene to give the C=N functionality. Although both singlet and triplet EtOCON are known to dehydrogenate NH–NH, CH–OH, and CH–CH groupings,[2] this is the first time that a similar dehydrogenation occurs on a CH–NH function.

(Ethoxycarbonyl)nitrene is reported to react with tertiary amines, the initial step being an electrophilic addition to an unshared electron pair on nitrogen. The resulting N–N ylides (aminimides) could be isolated only in some cases,[9] and we also reported a number of aminimides obtained from enamines.[3] *N,N*-Dimethylaniline[10] and *N*-methylmorpholine[11] gave products of nitrene insertion into the C–H bonds adjacent to the nitrogen atom, and N–N ylides have been claimed as intermediates in both cases.

In reactions performed in chloroform we found a strong dependence of reactivity upon concentration for all the tested substrates. While this behavior is not surprising for an ammonium salt that is supposed[6] to form reverse

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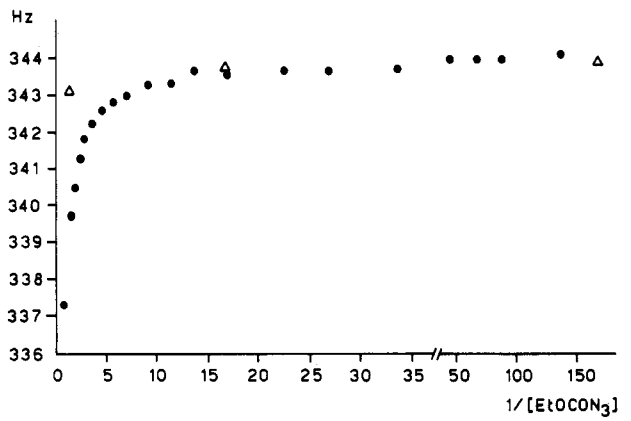

Figure 2. Chemical shift of the OCH_2 protons of $EtOCON_3$ in the absence (Δ) and in the presence (●) of DDA (in a fixed molar ratio DDA:$EtOCON_3$ = 1.5:1) vs. 1/[$EtOCON_3$] in $CDCl_3$ at 35 °C.

micelles under such conditions, it is unexpected for the amines, mainly the tertiary ones, that are known[12] to interact with chloroalkanes but, to the best of our knowledge, are not known to form any self-aggregate in chloroform.

We decided to test whether amines were aggregating under such conditions, and the ^1H NMR technique was used.

In Figure 1 we report the chemical shift of the protons of the dimethylamino group of DOA vs. the reciprocal concentration of DOA. The plot shows a behavior that is characteristic of self-aggregation phenomena.[6] The same dependence of the chemical shift upon the concentration of the solute has been observed in the case of DDA, and for DDA/ethyl azidoformate (in a fixed 1.5:1 ratio) on signals of both DDA and ethyl azidoformate. Ethyl azidoformate protons do not show any dependence of chemical shift upon the concentration of ethyl azidoformate but do depend upon DDA concentration (Figure 2). The results of these experiments indicate the existence of self-aggregating phenomena concerning DOA and DDA in chloroform. Ethyl azidoformate interacts with such aggregates but does not self-aggregate. The existence of these aggregates containing both amine and ethyl azidoformate can account for the formation of products of functionalization only above the concentration at which the reagents aggregate, while a well-defined geometry of such aggregate can account for the regioselectivity observed in this reaction.

Experimental Section

GC analyses were performed on a Carlo Erba 4100 gas chromatograph with a column of 3% SP 2250 (2 m × 2 mm) on 100/120 Supelcoport. Mass spectra (MS) were done on a Kratos MS 80, at an ionization potential of 70 eV. High-resolution mass spectra (HRMS) were obtained on a Kratos MS 80 spectrometer (15000 resolution). ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker WP 80 SY spectrometer with Me_4Si as an internal standard. Infrared spectra (IR) were obtained on a Perkin-Elmer 257 instrument. The separation by high-performance liquid chromatography (HPLC) was done on a Violet Clar 002 instrument, equipped with a Violet Clar 001 microprocessor and a variable-wavelength detector Violet Clar 004 (set at 254 nm). Solvents were HPLC grade. Dichloromethane and chloroform were distilled over $CaCl_2$. Ethyl azidoformate ($EtOCON_3$) was prepared from ethyl chloroformate and sodium azide.[13] *N,N*-Dimethyloctylamine (DOA)[14] and *N,N*-dimethyldodecylamine (DDA) (Fluka) were distilled over sodium wires. *N,N*-Dimethyloctylammonium propionate (DOAP) was obtained by reaction of DOA with propionic acid in hexane.[15]

Photolyses were carried out at room temperature in a quartz vessel using a medium-pressure Hanovia PCR lamp (100 W). The molar ratio between substrates (DOAP, DOA, DDA) (3 mmol) and $EtOCON_3$ (2 mmol) was always equal to 1.5. Substrate concentrations were 1.0, 0.1, and 0.04 M in chloroform or dichloromethane. After 3 h, the IR spectrum showed the disappearance of $EtOCON_3$, and the crude mixtures were washed with a 25% NaOH solution (in the case of propionate salt). The organic solvent was evaporated, and the residue was chromatographed on silica gel with a mixture of acetone and methanol (1:1) to remove the unreacted amine and ethyl urethane and then purified by HPLC using a Microporasil column (Waters) eluted with 20% isopropyl alcohol in hexane. All yields refer to chromatographically pure compounds and are based on $EtOCON_3$.

Photolyses in the Presence of DOAP. (i) Chloroform as Solvent. The reaction carried out at [DOAP] = 1.0 M gave (*Z,E*)-N^2-(ethoxycarbonyl)-N^1-methyl-N^1-octylformamidine (**1a**): 15%; IR ($CHCl_3$) 1675, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.3 (m + t, 15 H), (major isomer) 2.7 (s, 3 H, NCH_3), 2.8 (m, 2 H, NCH_2), 4.2 (q, 2 H, OCH_2), 9.0 (s, 1 H, HC=N), (minor isomer) 3.0 (s, 3 H, NCH_3), 3.3 (m, 2 H, NCH_2), 4.1 (q, 2 H, OCH_2), 8.5 (s, 1 H, HC=N); ^{13}C NMR ($CDCl_3$) δ 14.0 (chain CH_3), 14.5 (OCH_2CH_3), 22.6, 26.3, 28.1, 29.1 (3C), 31.7 (chain CH_2), (major isomer) 33.4 (NCH_3), 54.7 (NCH_2), 61.4 (OCH_2), 162.7 (HC=N), 164.6 (CO), (minor isomer) 39.2 (NCH_3), 47.7 (NCH_2), 61.4 (OCH_2), 163.0 (HC=N), 164.8 (CO); MS, *m/z* (relative intensity) 242 (M^+, 10), 227 (44), 213 (23), 197 (89), 171 (63), 157 (34), 144 (100), 130 (25); HRMS, 242.1993 (M^+), calcd for $C_{13}H_{26}N_2O_2$, 242.1994. The reactions carried out at [DOAP] = 0.1 and 0.04 M showed only the presence of byproducts and unreacted DOA with no detectable amounts of the product **1a**.

(ii) Dichloromethane as Solvent. The reaction carried out at [DOAP] = 1 and 0.04 M gave **1a** (45% and 30%, respectively).

Photolyses in the Presence of DOA. (i) Chloroform as Solvent. The reaction carried out at [DOA] = 1 M gave **1a** (27%). Only byproducts and unreacted DOA with no detectable amounts of **1a** were found at [DOA] = 0.1 and 0.04 M.

(ii) Dichloromethane as Solvent. The reaction carried out at [DOA] = 1 and 0.04 M gave **1a** (36% and 31%, respectively).

Photolyses in the Presence of DDA. (i) Chloroform as Solvent. The reaction carried out at [DDA] = 1 M gave (*Z,E*)-N^2-(ethoxycarbonyl)-N^1-methyl-N^1-dodecylformamidine (**1b**): 24%; IR (CCl_4) 1685, 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.3 (m + t, 23 H), (major isomer) 2.7 (s, 3 H, NCH_3), 2.8 (m, 2 H, NCH_2), 4.2 (q, 2 H, OCH_2), 9.0 (s, 1 H, HC=N), (minor isomer) 3.0 (s, 3 H, NCH_3), 3.3 (m, 2 H, NCH_2), 4.1 (q, 2 H, OCH_2), 8.3 (s, 1 H, HC=N); ^{13}C NMR ($CDCl_3$) δ 13.9 (chain CH_3), 14.4 (OCH_2CH_3), 22.6, 26.2, 28.1, 29.0, 29.2, 29.3, 29.5 (3 C), 31.8 (chain CH_2), (major isomer) 33.3 (NCH_3), 54.6 (NCH_2), 61.3 (OCH_2), 162.6 (HC=N), 164.5 (CO), (minor isomer) 39.2 (NCH_3), 47.7 (NCH_2), 61.3 (OCH_2), 162.9 (HC=N), 164.8 (CO); MS, *m/z* (relative intensity) 298 (M^+, 10), 283 (41), 269 (16), 253 (54), 226 (17), 171 (49), 157 (28), 144 (100), 130 (16); HRMS, 298.2619 (M^+), calcd for $C_{17}H_{34}N_2O_2$, 298.2620. The reactions carried out at [DDA] = 0.1 and 0.04 M showed only the presence of byproducts and unreacted DDA with no detectable amounts of the product **1b**.

(ii) Dichloromethane as Solvent. The reactions carried out at [DDA] = 1, 0.1, and 0.04 M gave **1b** (35%, 31%, and 24%, respectively).

Hydrolysis of 1. To 0.5 mmol of **1** in 1.5 mL of water and 3 mL of dioxane was added 0.5 mL of acetic acid, and the mixture was kept at 20 °C for 1 h. After workup only ethyl urethane and *N*-methyl-*N*-octylformamide (89%)[16] or *N*-dodecyl-*N*-methyl-

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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.

Acknowledgment. This work has been financially supported by the Consiglio Nazionale delle Ricerche (CNR, Roma), Progetto Finalizzato Chimica Fine e Secondaria.

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.

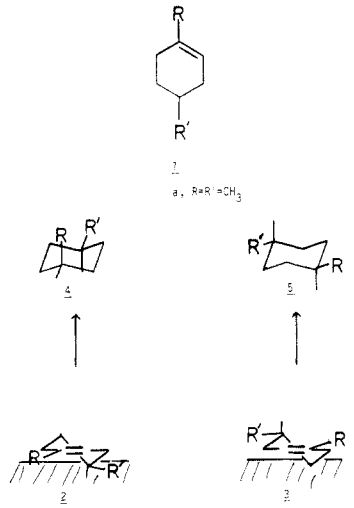
Heterogeneous Catalysis in Organic Chemistry. 7.[1] Stereochemistry of the Hydrogenation of 1,3,5-Trimethylcyclohexene

Robert L. Augustine* and Farrokh Yaghmaie

Department of Chemistry, Seton Hall University, South Orange, New Jersey 07079

Received October 20, 1986

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



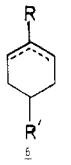
by hydrogen transfer from the catalyst surface to **2** is the *cis*-dialkylcyclohexane **4**. The trans product **5**, is obtained from the alternate adsorption mode, **3**. Published data[2,3] indicates that with **1a** there is an almost equal degree of hindrance between **2** and **3** with 57% of 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]

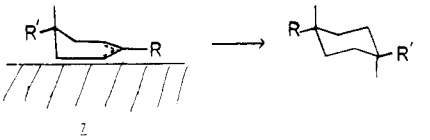
Table I. Percent Cis Product Formation on Hydrogenation of Methyl-Substituted Cyclohexenes

	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

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