Table I. Infrared Frequencies for Matrix-Isolated Species and Corresponding Known Compounds[a]

4	Me_2Si=CHMe[b]	5	$(MeSiHCH_2)_2$[c]
615 m	608	721 w	715 m
619 m			
	645	*d*	815 m
	708		
715 m	712	869 m	
			875 s
795 m	795	886 s	
			892 s
800 m		906 s	
812 m	808	945 s	
880 s		951 s	955 s
883 s	883	*d*	1260 m
888 s		1353 w	1355 w
986 s	978	2113 s	
1242 m		2116 s	
1254 m	1255	2134 s	2140 s
1295 w			
1298 w			
1315 w	1315		
	1370		
d	1410		
d	1450		
2191 s			
2198 s			

[a] In cm^{-1}. [b] Reference 4. [c] Room temperature spectrum.[6] [d] Bands in this region are masked by strong absorptions of **2** and **3**.

The lower spectrum shows a sample which has been photolyzed at 254 nm, bleached at 450 nm, and then annealed at 50 K for 15 min. The annealing sharpens the bands considerably and leads to the formation of new bands marked D, attributed to **5**, the cyclodimer of **4**. The observed bands agree fairly well with the room temperature infrared spectrum of authentic **5** (Table I).[6] Upon further annealing the bands due to **5** become strong while those of **4** completely disappear. Identification of **5** was confirmed by mass spectrometry which gave a parent peak at M = 116.

Similar bleaching of **1** upon irradiation with 450-nm light takes place in 3-methylpentane matrix at 77 K. Attempts were made to trap **4** with various reagents present in the matrix (methanol, 2,3-dimethyl-1,3-butadiene, and bis(trimethylsilyl)acetylene). However, complete photodestruction of **1** followed by annealing of the matrix at ~100 K led to the same products obtained for trapping of **1** under otherwise similar conditions, although in slightly lower yield.[7] A likely explanation is that thermal reversion of **4** to **1** is rapid at 100 K, and the latter is then trapped. At lower temperatures (50 K) thermal reversion is slowed and self-trapping of **4** takes place to form **5**. These experiments complement studies which show that thermolysis of **4** to **1** also takes place at high temperatures.[8]

Acknowledgment. Support of this work by Grant CHE-7850005 from the National Science Foundation and AF-AFOSR-78-3570 from the Air Force Office of Scientific Research is gratefully acknowledged.

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(6) Conlin, R. T. Ph.D. Thesis, Washington University, St. Louis, MO, 1976, p 96. Compound **5** is probably formed as a mixture of cis and trans isomers.

(7) At high trap concentrations, a significant amount of trapping occurs even during the initial photolysis, as indicated by the observation that the initially produced visible optical density due to **1** is lower. However it is impossible to account for the results by this mechanism alone. For instance, with 1% (v/v) v of triethylsilane in 3-methylpentane glass, the initial optical density due to **1** is 86% of that observed in pure 3-methylpentane. Under these conditions, (70 ± 5)% of **1** is trapped as 1,1-dimethyl-2,2,2-triethylsilane with or without bleaching by irradiation at 450 nm. With 10% (v/v) triethylsilane, the initial optical density due to **1** is only 36% of that observed in the pure solvent, and under these conditions, (80 ± 5)% of **1** is trapped with or without bleaching.

(8) Conlin, R. T.; Wood, D. L. *J. Am. Chem. Soc.* **1981**, *103*, preceding paper in this issue.

(9) **Note Added in Proof**: A recent calculation (Goddard, J. D.; Yoshioka, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1980**, *102*, 7644) predicts that the hydrogen shift $H_2Si{=}CH_2 \rightarrow HSiCH_3$ is approximately thermoneutral but that the activation energy is about 40 kcal/mol. Unless the additional methyl in **1** and **4** has a dramatic effect, this result is not compatible with our interpretation. No simple alternatives have occurred to us.

Stereochemical Aspects of the Nickel-Catalyzed Alkylation of Allylic Alcohols[1]

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It has recently been shown that Grignard reagents are able to alkylate allylic alcohols when nickel–phosphine complexes are used as the catalyst precursors.[2,3] Even though some stereochemical characteristics of the reaction have been investigated in relation to the synthesis of particular terpene derivatives,[4] the stereochemistry of the reaction is still unknown.

We have found that nickel–diphosphine complexes also are able to catalyze the alkylation of cyclic allylic alcohols such as 2-cyclohexen-1-ol.[5] We wish to report on the stereochemistry of the alkylation of *cis*- (**1a**) and *trans*-4-methyl-2-cyclohexen-1-ol (**1b**) by methylmagnesium iodide in the presence of [1,2-bis(diphenylphosphino)ethane]nickel(II) chloride.

cis-**1a** and *trans*-**1b** have been prepared, as has been previously reported,[6] through reduction of 4-methyl-2-cyclohexen-1-one with lithium aluminum hydride and separated on a highly efficient rectification column (auto annular still, Perkin Elmer 251). The alkylation reactions were carried out as we have previously reported.[5] The configurations of the olefins formed were established by hydrogenation in ethanol on Pt Adams catalyst at room temperature and atmospheric pressure to be those of the corresponding dimethylcyclohexanes (Scheme I). The isomeric composition of the alkylation products and the corresponding hydrogenated products was determined by capillary gas chromatography (100 M Squalane), which gave base line separation. The data obtained in the alkylation reactions are reported in Table I. They were reproducible within 1%.

These data show that the alkylation of allylic alcohols by Grignard reagent in the presence of nickel–diphosphine catalysts is stereospecific and takes place on the side of the ring opposite to that of the replaced hydroxyl group (anti attack).[7] The minor amount of the alternative diastereomeric alkylation product corresponds indeed to the diastereomeric purity of the starting material.

The regioselectivity for alkylation at the α or γ position (position 1 or 3, respectively, in the starting material) for the two diastereomeric 4-methyl-2-cyclohexen-1-ols is remarkably different. As

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(1) Dedicated to Professor Dr. P. Pino on the occasion of his 60th birthday.

(2) C. Chuit, H. Felkin, C. Frajerman, G. Roussi, and G. Swierczewski, *J. Organomet. Chem.*, **127**, 371 (1977).

(3) H. Felkin, E. Jampel-Costa, and G. Swierczewski, *J. Organomet. Chem.*, **134**, 265 (1977).

(4) B. L. Buckwalter, I. R. Burfitt, H. Felkin, M. Joly-Goudket, K. Naemura, M. F. Salomon, E. Wenkert, and P. M. Wovkulich, *J. Am. Chem. Soc.*, **100**, 6445 (1978).

(5) G. Consiglio, F. Morandini, and O. Piccolo, *Helv. Chim. Acta*, **63**, 987 (1980).

(6) A. L. J. Beckwith and G. Phillipou, *Aust. J. Chem.*, **29**, 1277 (1976).

(7) A referee called our attention to the fact that predominant inversion of configuration has been found in the alkylation of (+)-1-buten-3-ol by C_6H_5MgBr in the presence of $(Ph_3P)_2NiCl_2$ (M. Joly-Goudket, Thesis, Université de Paris-Sud, Orsay, France, 1972, cited in a footnote, p 379 of ref 2).

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Scheme I

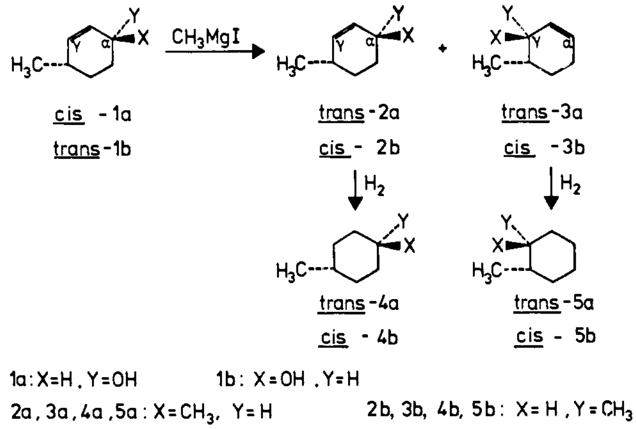
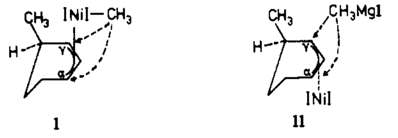


Table I. Isomeric Product Composition in the Alkylation of *cis*- (**1a**) and *trans*-4-Methyl-2-cyclohexen-1-ol (**1b**)

starting product (diastereomeric purity, %)	isomeric product composition, %			
	trans-**2a**	*trans*-**3a**	*cis*-**2b**	*cis*-**3b**
cis-**1a** (99)	52.5	46.5	1	0
trans-**1b** (98)	1	1	88	10

Chart I. Possible Intermediates in the Alkylation of *trans*-**1b**



a matter of fact the ratio of α to γ attack is 1.1 for *cis*-**1a** and 8.8 for *trans*-**1b**.

Reasonable arguments have been presented that the nickel-catalyzed alkylation of allylic alcohols with Grignard reagents proceeds via a π-allylnickel intermediate.[8,9] Such an intermediate is further supported by the fact that in the enantiomer discriminating alkylation by methylmagnesium iodide of racemic 2-cyclohexen-1-ol[5] catalyzed by [(−)-(*R*)-1,2-bis(diphenylphosphino)-1-phenylethane]nickel(II) chloride, the optical purity of the recovered alcohol depends on the extent of conversion whereas that of the 3-methylcyclohexene formed does not.[10] With the assumption of a π-allyl intermediate, the observed stereochemistry can be the result of two different pathways: (i) formation of an allyl nickel intermediate with anti attack and alkyl transfer on the frontside of the π-allyl system with respect to the nickel atom (Chart I, I); (ii) formation of the π-allyl species with syn stereochemistry followed by exo attack of the Grignard reagent (Chart I, II). Both possibilities can account for the difference in regioselectivity (α:γ attack ratio) found in the alkylation of *cis*-**1a** and *trans*-**1b**. As a matter of fact, the attack at the γ position is sterically less favored than at the α position; this difference is even greater when the methyl group on the ring is syn rather than anti with respect to the incoming nucleophile. It is worthwhile to note that the same stereochemistry and similar regioselectivity have been found for the copper-catalyzed alkylation of allylic ethers by Grignard reagents.[11]

Work is in progress with the aim of isolating diastereomeric allyl nickel complexes related to the proposed intermediate and to distinguish if possibility i or ii is in effect.

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(8) H. Felkin and G. Swierczewski, *Tetrahedron Lett.*, 1433 (1972).

(9) J. K. Kochi, "Organometallic Mechanisms and Catalysis", Academic Press, New York, 1978, p 404 *ff.*

(10) G. Consiglio, F. Morandini, and O. Piccolo, "Abstract of Papers", 2nd international Symposium on Homogeneous Catalysis, Sept 1-3, 1980, Düsseldorf, Germany, p 154.

(11) Y. Gendreau and J. F. Normant, *Tetrahedron*, **35**, 1517 (1979).

Stoichiometric Decarbonylation of Benzoyl Chloride by Chlorotris(triphenylphosphine)rhodium(I)[1]

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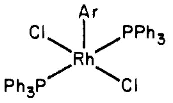
Some think that the stoichiometric (30–100 °C) and catalytic (~180 °C) decarbonylations of benzoyl chloride by $RhCl(PPh_3)_3$ proceed by comparable mechanisms to give the same products, chlorobenzene and $RhCl(CO)(PPh_3)_2$.[2] The difference between the stoichiometric and catalytic reactions is simply attributed to the lack of further reactivity of $RhCl(CO)(PPh_3)_2$ at low temperatures.[3] These views are based, in part, on a analogy to the decarbonylations of other nonaromatic acid chlorides and are summarized by Scheme I. In addition, there is a direct report[4] that $RhCl(PPh_3)_3$ reacts with benzoyl chloride in benzene (80 °C, 15 min) to give high yields of chlorobenzene and $RhCl(CO)(PPh_3)_2$ and a reported kinetic study[5] of the low-temperature decomposition of an isolated intermediate, $RhCl_2(CO)(Ph)(PPh_3)_2$ (**3a**), to give the same products. We now report that the stoichiometric decarbonylation of benzoyl chloride by $RhCl(PPh_3)_3$ at low temperatures does not give chlorobenzene; the aryl-containing product of the reaction is $RhCl_2(Ph)(PPh_3)_2$ (**5a**). The thermal decomposition of isolated $RhCl_2(CO)(Ph)(PPh_3)_2$ (**3a**), also gives the same complex **5a** and does not give chlorobenzene.



5a,b

The reaction of $RhCl(PPh_3)_3$ with excess benzoyl chloride for 15 min at 80 °C according to the literature procedure[4] gave a yellow precipitate which was readily identified as $RhCl_2(CO)(Ph)(PPh_3)_2$ (**3a**), identical in all respects to an authentic sample.[5-7] Further workup of the filtrate[8a] showed that neither chlorobenzene[8b] nor $RhCl(CO)(PPh_3)_2$ (IR, 1968 cm^{-1}) had been formed.

Since $RhCl_2(CO)(Ph)(PPh_3)_2$ is thought[3,5] to be an intermediate on the path to chlorobenzene and $RhCl(CO)(PPh_3)_2$, the reaction described above was simply continued for longer reaction times (24–96 h). Alternatively, complex **3a** was isolated, purified, and reintroduced to a benzene solution of benzoyl chloride at 80 °C. These two experiments differ with respect to 1 equiv of free PPh_3

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(1) Taken, in part, from the Ph.D thesis of J. B. Philip, Jr., University of Rochester, NY, 1980.

(2) These reactions are cited in many textbooks and monographs: Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980; pp 90–92. Heck, R. F., "Organotransition Metal Chemistry"; Academic Press: New York 1974; pp 264–265. The literature has been summarized and reviewed several times, most recently and thoroughly by Baird (Baird, M. C. In "The Chemistry of Acid Derivatives"; Patai, S., Ed., Wiley: New York, 1979; Supplement B, Part 2, pp 825–857. See also: Tsuji, J. In "Organic Synthesis by Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, pp 595–654.

(3) We do not mean to specify, in detail, how $RhCl(CO)(PPh_3)_2$ reenters the cycle. Proposals range from a direct reaction with acid chloride[3a] to initial loss of phosphite[3b] to initial loss of CO.[3c] Others have proposed that $RCl(CO)(PPh_3)_2$ is not even involved.[3d] (a) Ohno, K.; Tsuji, J. *J. Am. Chem. Soc.* **1968**, *90*, 99–107. (b) Stille, J. K.; Huang, F.; Regan, M. T. *Ibid.* **1974**, *96*, 1518–1522. (c) Strohmeier, W.; Pföhler, P. *J. Organomet. Chem.* **1976**, *108*, 393–399. (d) Blum, J.; Oppenheimer, E.; Bergmann, E. D. *J. Am. Chem. Soc.* **1967**, *89*, 2338–2341.

(4) Blum, J. *Tetrahedron Lett.* **1966**, 1605–1608.

(5) Stille, J. K.; Regan, M. T. *J. Am. Chem. Soc.* **1974**, *96*, 1508–1514.

(6) Baird, M. C.; Mague, J. T.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 1347–1360.

(7) That is, mp, IR, ^{1}H NMR, and ^{31}P NMR. The IR absorption at 2070 cm^{-1} and the Rh–^{31}P coupling constant, J = 88.5 Hz, are diagnostic for Rh(III)–CO complexes. See: Slack, D. A.; Egglestone, D. L.; Baird, M. C. *J. Organomet. Chem.* **1978**, *146*, 71–76.

(8) (a) The filtrate was separated into volatile and nonvolatile fractions by bulb-to-bulb distillation in vacuo and analyzed by gas chromatography and IR spectroscopy, respectively. (b) A 1% yield was readily detectable by GC.

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