References and Notes

(1) Part 7: J. Banville and P. Brassard, *J. Chem. Soc., Perkin Trans. 1*, in press.

(2) J. Banville, J.-L. Grandmaison, G. Lang, and P. Brassard, *Can. J. Chem.*, **52**, 80 (1974).

(3) K. C. Brannock, R. D. Burpitt, and J. G. Thweatt, *J. Org. Chem.*, **28**, 1697 (1963).

(4) B. S. Joshi, S. Ramanathan, and K. Venkataraman, *Tetrahedron Lett.*, 951 (1962).

(5) W. Steglich and W. Reininger, *Chem. Commun.*, 178 (1970).

(6) J. K. K. Lam and M. V. Sargent, *J. Chem. Soc., Perkin Trans. 1*, 1417 (1974).

(7) B. Franck, U. Ohnsorge, and H. Flasch, *Tetrahedron Lett.*, 3773 (1970).

(8) A. Castonguay and P. Brassard, *Synth. Commun.*, **5**, 377 (1975). (Other methods of preparation will be communicated shortly.)

(9) B. Franck and I. Zimmer, *Chem. Ber.*, **98**, 1514 (1965).

(10) D. B. Bruce and R. H. Thomson, *J. Chem. Soc.*, 1089 (1955).

(11) P. C. Arora and P. Brassard, *Can. J. Chem.*, **45**, 67 (1967).

(12) T. F. Low, R. J. Park, M. D. Sutherland, and I. Vessey, *Aust. J. Chem.*, **18**, 182 (1965).

(13) I. Singh, R. E. Moore, C. W. J. Chang, R. T. Ogata, and P. J. Scheuer, *Tetrahedron*, **24**, 2969 (1968).

(14) A. McKillop, B. D. Howarth, and R. J. Kobylecki, *Synth. Commun.*, **4**, 35 (1974).

(15) S. M. McElvain, H. I. Anthes, and S. H. Shapiro, *J. Am. Chem. Soc.*, **64**, 2525 (1942). (In this procedure benzene is advantageously replaced by xylene.)

(16) S. T. D. Gough and S. Trippett, *J. Chem. Soc.*, 2333 (1962).

(17) C. Moureu and R. Delange, *Bull. Soc. Chim. Fr.*, **29**, 648 (1903).

(18) Y. Asahina and F. Fujikawa, *Chem. Ber.*, **68**, 1558 (1935).

(19) K. Venkataraman, *J. Sci. Ind. Res.*, **25**, 97 (1966).

(20) V. H. Powell and M. D. Sutherland, *Aust. J. Chem.*, **20**, 541 (1967).

Nickel-Promoted Isomerizations of Alkenes Bearing Polar Functional Groups

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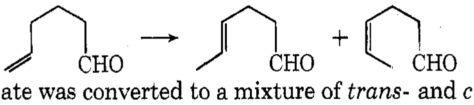
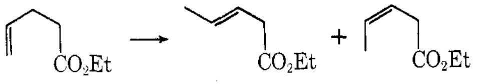
A catalyst derived from ethylenebis(tri-*o*-tolyl phosphite)nickel(0) (1) and hydrogen chloride has been found to isomerize a variety of alkenes bearing polar functional groups. Treatment of 5-hexenal and ethyl 4-pentenoate with the catalyst in hexane or toluene solution at 25 °C afforded essentially quantitative yields of the geometric isomer mixtures of 4-hexenal and of ethyl 3-pentenoate, respectively. High-yield catalytic conversions of 5-chloro-1-pentene and of 4-penten-1-ol to 5-chloro-2-pentene and 3-penten-1-ol, respectively, were also achieved. The configurationally specific conversion of allyl phenyl ether to phenyl *cis*-propenyl ether was accomplished in high yield. A number of allylic alcohols were isomerized to saturated carbonyl compounds by 1 and HCl. Allyl alcohol, 1-hexen-3-ol, 2-cyclohexen-1-ol, 2-methyl-2-propen-1-ol, 3-penten-2-ol, 2-buten-1-ol, and 1,4-pentadien-3-ol were converted to propanal, 3-hexanone, cyclohexanone, 2-methylpropanal, 2-pentanone, 1-butanal, and penten-3-one, respectively. The ethylenebis(tri-*o*-tolyl phosphite)nickel(0)–hydrogen chloride system catalyzed the skeletal rearrangement of *cis*-1,4-hexadiene to *trans*-2-methyl-1,3-pentadiene in 1-butanol and ethyl hexanoate solvents. This transformation was accompanied by the formation of *cis,cis*- and *trans,cis*-2,4-hexadienes. Treatment of 2,5-hexadien-1-ol with the catalyst system in hexane solvent afforded *trans*-4-methyl-2,4-pentadien-1-ol as major product along with lesser amounts of 5-hexenal. When 2,5-hexadien-1-ol was treated with the catalyst in ethylene-saturated hexane, *trans*-4-methyl-2,4-pentadien-1-ol, 5-hexenal, *cis*-4-hexenal, and *cis,cis*-2,4-hexadien-1-ol were formed.

Soluble nickel-based catalysts can promote double bond positional isomerizations of simple alkenes[1] and polyenes[1c,2] as well as skeletal isomerizations of certain dienes.[2a,3] While the reactions of afunctional alkenes have been studied quite extensively, the applicability of the catalysts to isomerizations of alkenes bearing polar functional groups has not received much attention. In some cases, the natures of the catalyst precursors have been responsible for the limited scope of inquiry. For instance, the first catalysts which were found to cleave carbon–carbon σ bonds in dienes to afford rearranged products were derived from in situ reactions of nickel(II) complexes with alkylaluminum compounds.[2a,3] The aluminum cocatalysts react with most polar functional groups. Our findings that catalysts derived from ethylenebis(triarylphosphine)nickel(0) complexes and hydrogen halides accomplish both the 1,4-pentadiene to isoprene type rearrangement and alkene double bond migration reactions[3-5] offered the probability that isomerizations of functionally substituted alkenes could be achieved. The compatibility of this type of catalyst system with polar molecules was demonstrated by the successful isomerization of *cis*-1,4-hexadiene by ethylenebis(tri-*o*-tolyl phosphite)nickel(0) (1) and hydrogen chloride in 1-butanol solvent. During 5 min at room temperature, *trans*-2-methyl-1,3-pentadiene and *trans,cis*- and *cis,cis*-2,4-hexadienes were afforded in 26, 6, and 26% yields, respectively, at 78% conversion of the 1,4-diene to products when a 12:1:0.8 diene:Ni:HCl molar ratio was employed. Comparable results were obtained when ethyl hexanoate solvent was used. These results induced our discovery that a variety of alkenes bearing polar functional groups could be isomerized in high yield by the 1/HCl catalyst system.

Treatment of 5-hexenal with 1 and HCl in toluene or hexane solvents afforded essentially quantitative yields of *trans*- and *cis*-4-hexenal at 100% conversion when aldehyde:Ni ratios as high as 50:1 were employed, eq 1. In a like manner, ethyl 4-pentenoate was converted to a mixture of *trans*- and *cis*-ethyl 3-pentenoate in quantitative yield at 83% conversion, eq 2.



(1)



(2)

These reactions are synthetically useful since α,β-unsaturated carbonyl compounds are not generated, but the double bond migration can be controlled to produce nonconjugated products. High-yield catalytic isomerizations of 5-chloro-1-pentene and of 4-penten-1-ol were also achieved.

The configurationally specific catalytic generation of an enol ether from allyl phenyl ether was demonstrated, eq 3.

(3)

Table I. Alkene Isomerization Reactions Catalyzed by 1/HCl[a]

Expt	Registry no.	Alkene reactant	Reaction time, h	% conversion	Alkene products[b] % yield Trans	Alkene products[b] % yield Cis
1	764-59-0	5-Hexenal[c,d]	0.5	100	60	40
2		5-Hexenal[c]	1.0	96	53	45
3	1968-40-7	Ethyl 4-pentenoate	0.5	83	58	44
4	928-50-7	5-Chloro-1-pentene	0.5	95	55	45
5	821-09-0	4-Penten-1-ol	0.5	93	58	28
6	1746-13-0	Allyl phenyl ether	0.5	34	0	83

[a] Unless noted otherwise, all experiments were conducted under argon in dry deoxygenated hexane solutions at 25 °C with an alkene/Ni/HCl ratio of 50.0:1.0:0.8. [b] Experiment 1, 4-hexenal; 2, 4-hexenal; 3, ethyl-3-pentenoate; 4, 5-chloro-2-pentene; 5, 3-penten-1-ol; 6, phenyl propenyl ether. [c] The experiment was conducted in dry deoxygenated toluene. [d] Alkene/Ni/HCl ratio was 20.0:1.0:0.8.

Table II. Rearrangements of Allylic Alcohols by 1/HCl[a]

Registry no.	Alcohol	Time	Solvent	ROH/Ni/HCl	% conversion	% yield	Product
107-18-6	Allyl alcohol[b]	5 days	Xylene	20.0/1.0/0.8	100	100	Propanal
4978-44-1	1-Hexen-3-ol	2 days	Xylene	2.0/1.0/0.8	100	81	3-Hexanone
	1-Hexen-3-ol[c]	11 days	Xylene	20.0/1.0/0.8	99	74	3-Hexanone
822-67-3	2-Cyclohexen-1-ol	1 h	Pentane	2.0/1.0/1.0	26	51	Cyclohexanone
	2-Cyclohexen-1-ol	1 h	Et_2O	2.0/1.0/1.0	37	20	Cyclohexanone
513-42-8	2-Methyl-2-propen-1-ol	1 h	Toluene	2.0/1.0/0.8	65	30	2-Methylpropanal
	2-Methyl-2-propen-1-ol	1 h	Toluene	10.0/1.0/0.8	20	29	2-Methylpropanal
1569-50-2	3-Penten-2-ol[d]	1 h	Pentane	2.0/1.0/1.0	92	64	2-Pentanone
	3-Penten-2-ol[d]	1 h	Toluene	2.0/1.0/1.0	95	40	2-Pentanone
6117-91-5	2-Buten-1-ol[e]	2 h	Et_2O	5.0/1.0/1.0	79	33	Butanal
	2-Buten-1-ol[e]	2 h	Et_2O	2.0/1.0/1.4	98	80	Butanal
922-65-6	1,4-Pentadien-3-ol	1 h	Hexane	2.0/1.0/0.8	63	20	Penten-3-one

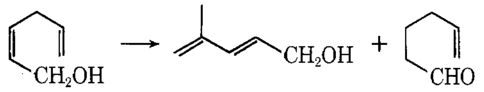
[a] Unless otherwise noted all reactions were conducted under argon in dry dexoygenated solvent at 25 °C. [b] 45 °C. [c] Reaction temperature was 50 °C. [d] 97% trans, 3% cis. [e] 95% trans, 5% cis.

Phenyl *cis*-propenyl ether was afforded in 83% yield at 34% conversion by the 1/HCl catalyst during 30 min in hexane. No trans isomer was detected in the product mixture. Yield and conversion data and descriptions of reaction conditions for these experiments are presented in Table I.

Although no attempt has been made to determine the maximum alkene:Ni ratio that is operable for each transformation described in Table I, experiments employing 5-chloro-1-pentene indicated that the achievable percent conversions decreased with increasing alkene:Ni ratio. Under conditions comparable to those given in Table I, 26% of 5-chloro-1-pentene was converted to 5-chloro-2-pentene in 98% yield when a 200:1 alkene:Ni ratio in hexane was used. An 82% yield of 5-chloro-2-pentene was afforded at 13.5% conversion in neat 5-chloro-1-pentene when a 1000:1 alkene:Ni ratio was employed. These data correspond to 51 and 111 catalytic cycles, respectively.

Only a few examples of the conversion in solution of allylic alcohols to saturated carbonyl compounds by transition metal complexes are known.[6] The capability of the 1/HCl system to accomplish such transformations was therefore investigated. Alcohols possessing unsubstituted double bonds were slowly converted in high yield to saturated carbonyl compounds when alcohol:Ni molar ratios as high as 20:1 were employed. The catalyst was not long lived in reactions of substituted allylic alcohols. While the initial rates of reaction were relatively high, the catalyst became deactivated during a 2-h period and only moderate yields of carbonyl products were afforded, even when very low alcohol:Ni ratios were employed. Data from these experiments are tabulated in Table II.

Treatment of 2,5-hexadien-1-ol with 1 and HCl (dienol: Ni:HCl, 5.0:1.0:0.8) afforded a skeletally isomeric alcohol as the major product along with lesser amounts of double bond migration products. During ca. 30 min in hexane solvent at 24–26 °C, 73–80% conversions of hexadienol to products were achieved and *trans*-4-methyl-2,4-pentadien-1-ol and 5-hexenal were formed in 30–40 and 7–10% yields, respectively, in a series of experiments, eq 4. Higher yields of the skeletal rearrangement product could be achieved when the experiments were conducted in ethylene-saturated hexane. Under this modified condition, 73% of the dienol was converted to product during ca. 30 min and *trans*-4-methyl-2,4-pentadien-1-ol, 5-hexenal, *cis*-4-hexenal, and *cis,cis*-2,4-hexadien-1-ol were afforded in 67, 6, 5, and 20% yields, respectively.



(4)

Previous studies of the 1/HCl and related catalyst systems indicate that the hydrogen transfer that accompanies these isomerizations should occur by a nickel hydride–alkene addition–elimination sequence.[1b,1e,3] The saturated carbonyl compounds which are generated from allylic alcohols would, therefore, be formed via enol intermediates. The generation of an enol ether from allyl phenyl ether supports this picture.

Experimental Section

All experiments employing ethylenebis(tri-*o*-tolyl phosphite)-nickel(0) were conducted under an argon atmosphere in deoxygenated solvents. Proton magnetic resonance spectra were recorded on a Varian A-60 instrument using tetramethylsilane as an internal standard in carbon tetrachloride solvent. Infrared spectra were obtained on a Beckman IR-12 spectrophotometer and mass spectra were recorded on a Du Pont 21-491 spectrometer.

Reaction solvents were dried over sodium–benzophenone and then distilled. All functionalized alkenes except 5-hexenal, ethyl 4-pentenoate, 1,4-pentadien-3-ol, and *cis*-2,5-hexadiene-1-ol were commercially available. 5-Hexenal was prepared from the commercially available 5-hexen-1-ol by the method of Sheikh and Eadon.[7] Ethyl 4-pentenoate,[8] 1,4-pentadien-3-ol,[9] and *cis*-2,5-hexadien-1-ol[10] were also prepared by literature procedures. *cis*-1,4-Hexadiene was prepared by the procedure of Hata.[11] Ethylenebis(tri-*o*-tolyl phosphite)nickel(0) was prepared by the method of Seidel and Gosser.[12]

Typical Procedures for Alkene Isomerization Experiments. An ether solution, 0.08 ml, containing 0.065 mmol of hydrogen chloride was transferred via hypodermic syringe to a flask containing 0.081 mmol of ethylenebis(tri-*o*-tolyl phosphite)nickel(0) (1). 5-Chloro-1-pentene, 4.06 mmol, in 3 ml of hexane was then added to the amber-colored solution affording a solution that was orange-amber in color. The mixture was stirred under argon at room temperature and within 15 min, the color of the reaction solution had faded to a cloudy pale yellow. Thirty-microliter aliquots were removed periodically; they were quenched by exposure to air, and then analyzed by GLC on a 10 ft × 0.25 in., 20%, 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb W column. On termination of an experiment, the volatile organic material was removed from the reaction flask in vacuo. The resulting hexane solution was then concentrated by distillation after which the reaction products were collected by preparative GLC.

Experiments involving other functionalized alkenes were conducted in a similar manner with the following exceptions. Isomerization reactions of all allylic alcohols except 1,4-pentadien-3-ol and *cis*-2,5-hexadien-1-ol were accomplished by adding the hydrogen chloride solution to a solution of **1**, the allyl alcohol, and the solvent. When 2,5-hexadien-1-ol was treated with 1 and HCl in the presence of ethylene, an ethylene-saturated solution of the alcohol in hexane was added to the flask containing 1 and HCl in ether–hexane. Ethylene was then passed through the reaction mixture for 5 min.

Product mixtures derived from reactions of allylic alcohols were analyzed by GLC on a 6 ft × 0.25 in. 20% Carbowax 20M on Chromosorb P column.

Determination of Product Yields. Percent conversions were based upon consumed alkene reactant and percent yields were defined as the percent of consumed starting material that was transformed into each product. Yield and conversion data were determined by GLC. In experiments employing allylic alcohols, standard mixtures of reactants and products were analyzed in order to determine the relationships between signal responses and molar amounts present. In each case, a known quantity of an internal standard, *m*-xylene, mesitylene, benzene, or *n*-hexane, was used, the choice depending upon the retention times of the reactants and products. Ratios of GLC peak areas were assumed to represent molar ratios of reactants and products in experiments involving double bond migrations in functionalized alkenes where the type of functional group was the same in both reactant and products.

It was found that the signal responses per mole of 2-buten-1-ol, 2-cyclohexen-1-ol, and 2,5-hexadien-1-ol decreased with increased time of use of the Carbowax 20M column. This situation was rectified by the periodic replacement of a portion of the column at the injection end with fresh Carbowax 20M on Chromosorb P packing. A 4-in. column extension was utilized for this purpose. It was necessary to monitor the column deterioration by periodic analyses of standard reactant–product mixtures.

Product Identifications. The structure assignments of the products described in Table I were based upon examination of the ^{1}H NMR, infrared, and mass spectra of each compound after isolation by preparative GLC. The parent ion peak in the mass spectrum of each compound corresponded with the assigned molecular weight. The multiplicities and chemical shifts of the proton resonances along with the ^{1}H NMR integrations were all consistent with the assigned structures. The geometry of the internal double bond was established by the alkene C–H out-of-plane deformation vibration, found near 10.3–10.42 μ for the trans isomers and 14.28–14.60 μ for the cis isomers.[1c,13] The GLC retention time of the cis isomer was found to be longer than that of the trans isomer in each case. The magnitude of the vinyl proton–proton coupling constant, $J_{\mathrm{H-H}} = 6.2$ Hz, in phenyl *cis*-propenyl ether was used as a criterion for its configuration.[14]

The aldehyde and ketone products described in Table II were identified by comparisons of their ^{1}H NMR spectra and GLC retention times with those of authentic samples.

The identity of the skeletal rearrangement product derived from *cis*-2-5-hexadien-1-ol was established by its ^{1}H NMR, infrared, and mass spectra. The trans configuration of the internal double bond was evident from the strong band at 10.31 μ and from the magnitude of the alkene proton–proton coupling constant, $J_{\mathrm{H-H}} = 16.0$ Hz, for the internal double bond protons. The configuration in *cis,cis*-2,4-hexadien-1-ol was established by comparing its ^{1}H NMR spectrum with that of *cis,cis*-2,4-hexadiene. The mass spectrum indicated the appropriate parent ion mass.

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References and Notes

(1) (a) Y. Chauvin and G. Lefebvre, *C. R. Acad. Sci.*, **259**, 2105 (1964); (b) R. Cramer and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **88**, 3534 (1966); (c) R. G. Miller, T. J. Kealy, and A. L. Barney, *ibid.*, **89**, 3756 (1967); (d) B. Corain, *Chem. Ind. (London)*, 1465 (1971); (e) C. A. Tolman, *J. Am. Chem. Soc.*, **94**, 2994 (1972); (f) B. Corain and G. Puosi, *J. Catal.*, **30**, 403 (1973); (g) G. Strukul, M. Bonivento, R. Ros, and M. Graziani, *Tetrahedron Lett.*, 1791 (1974); (h) R. G. Miller, D. R. Fahey, H. J. Golden, and L. C. Satek, *J. Organomet. Chem.*, **82**, 127 (1974).

(2) (a) R. G. Miller, *J. Am. Chem. Soc.*, **89**, 2785 (1967); (b) E. N. Kropacheva, B. A. Dologoplosk, I. I. Ermakova, I. G. Zhuchikhina, and I. Y. Tsereteli, *Dokl. Akad. Nauk SSSR*, **187**, 1312 (1969).

(3) R. G. Miller, P. A. Pinke, R. D. Stauffer, H. J. Golden, and D. J. Baker, *J. Am. Chem. Soc.*, **96**, 4211 (1974), and references cited therein.

(4) R. G. Miller, P. A. Pinke, R. D. Stauffer, and H. J. Golden, *J. Organomet. Chem.*, **29**, C42 (1971).

(5) See L. W. Gosser and G. W. Parshall, *Tetrahedron Lett.*, 2555 (1971), for related findings.

(6) For examples and for background information see (a) G. F. Emerson and R. Pettit, *J. Am. Chem. Soc.*, **84**, 4591 (1962); (b) R. W. Goetz and M. Orchin, *ibid.*, **85**, 1549 (1963); (c) J. K. Nicholson and B. L. Shaw, *Proc. Chem. Soc., London*, 282 (1963); (d) W. T. Hendrix, F. G. Cowherd, and J. L. von Rosenberg, *Chem. Commun.*, **97**, (1968); (e) H. C. Clark and H. Kurosawa, *J. Chem. Soc., Chem. Commun.*, 150 (1972); J. Hillis, J. Francis, M. Ori, and M. Tsutsui, *J. Am. Chem. Soc.*, **96**, 4800 (1974).

(7) M. Y. Sheikh and G. Eadon, *Tetrahedron Lett.*, 257 (1972).

(8) (a) C. S. Marvel and F. D. Hager, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1941, p 248; (b) J. J. Ritter and T. J. Kaniecki, *J. Org. Chem.*, **27**, 622 (1962).

(9) H. E. Ramsden J. R. Leebrick, S. D. Rosenberg, E. H. Miller, J. J. Walburn, A. E. Balint, and R. Cserr, *J. Org. Chem.*, **22**, 1602 (1957).

(10) J. M. Shackelford, W. A. Michalwicz, and L. H. Schwartzman, *J. Org. Chem.*, **27**, 1631 (1962).

(11) G. Hata, *J. Am. Chem. Soc.*, **86**, 3903 (1964).

(12) W. C. Seidel and L. W. Gosser, *Inorg. Synth.*, **15**, 9 (1974).

(13) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds", Wiley, New York, N.Y., 1963, p 59.

(14) H. J. Golden, D. J. Baker and R. G. Miller, *J. Am. Chem. Soc.*, **96**, 4235 (1974).