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NICKEL-CATALYZED ALLYL-TRANSFER REACTIONS

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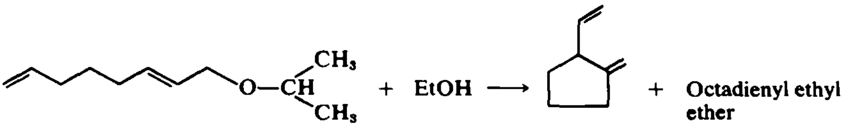
Abstract—The reaction of allylic compounds in the presence of some nickel catalysts has been studied. 2,7-Octadienyl isopropyl ether is converted into 2-methylenevinylcyclopentane in moderate yield by $NiX_2(n\text{-}Bu_3P)_2$–t-BuOK (1:2) (where X is Cl, Br, or NO_3) in ethanol. In amines the hydroxyl or ether group of allyl compound is smoothly substituted with the amino group; corresponding allyl substituted amines are formed in high yields. Allyl alcohol is selectively converted to diallyl ether in the presence of $Ni(Acac)_2$–n-Bu_3P–$NaBH_4$ (1:3:1) at 40°C. At higher temperature isomerization of allyl alcohol into propionaldehyde is predominate. These reactions are considered to proceed through π-allyl intermediates.

Compounds having a mobile group at an allylic position, such as allyl halides or allyl alcohol, react with transition metals to form isolable π-allyl complexes.[1] To elucidate the mechanism of transition metal-catalyzed reaction of olefins, a variety of transiently formed π-allyl complexes was also proposed.[2] In the course of our study of the synthesis of 2-methylenevinylcyclopentane (MVCP) from the dimerization of butadiene,[3] it was found that in the presence of $(n\text{-}Bu_3P)NiBr_2$–RONa 2,7-octadienyl ether is converted into MVCP in moderate yield. This observation suggests that some groups at the allylic position are easily eliminated and nickel-carbon bond, i.e., a π-allyl nickel intermediate, is transiently formed. π-Allyl nickel is a versatile reagent in synthetic organic chemistry, since it reacts with various compounds.[4] This success in converting 2,7-octadienyl ether into MVCP (Eq 1) encouraged us to study the substitution reaction (Eq 2) of some allyl groups,[5,6] which is assumed to proceed through a π-allyl nickel.

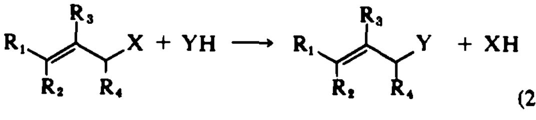
(a) *Reaction of* 2,7-*Octadienyl Ether.* In this reaction bis(tri-n-butylphosphine)nickel nitrate, combined with potassium-t-butoxide, was used as a catalyst. The reaction (Eq 1) proceeded smoothly in ethanol at 80°C.


(1)

The catalytic activity depends upon the concentration of potassium t-butoxide, the effect of which is shown in Fig 1. A ratio of alkoxide to Ni, around 2:1, gave the best result for the formation of MVCP. The other products were isomeric octadienyl ethyl ethers; the substitution of isopropyl group by ethoxy group occurred considerably. On the other hand, when 2,7-octadienyl ethyl ether was allowed to react under similar conditions, no appreciable elimination product of the allyl group was obtained, but only isomerization of the double bond occurred predominantly.

Nickel complexes $(n\text{-}Bu_3P)_2NiX_2$ other than the nitrate were also effective. The activity for the formation of MVCP increases in the order: nitrate > bromide > chloride. When 2 moles of the alkoxide were used, a zero-valent nickel, which is capable of forming a π-allyl complex through oxidative addition, is considered to be formed.[7] Addition of more alkoxide results in the base-catalyzed isomerization of the double bonds before the oxidative addition.[8]

(b) *Substitution Reaction of Allyl Group.* The reaction (Eq 2) was


(2)

R = H or alkyl

proved to be highly satisfactory and the yields were high. The results are summarized in Table 1. The reaction depends on the leaving groups and on the reagents such as amine, thiol or alcohol. That this substitution reaction proceeds through a π-allyl intermediate was confirmed by the reaction of 1-octen-3-ol with morpholine, to give N-(2-octenyl)morpholine. The formation of this compound suggests that the substitution occurred at less crowded terminal position of the π-allyl group. No appreciable reaction occurred with aniline, ethylene imine, pyrollidone or aldehyde. When di-

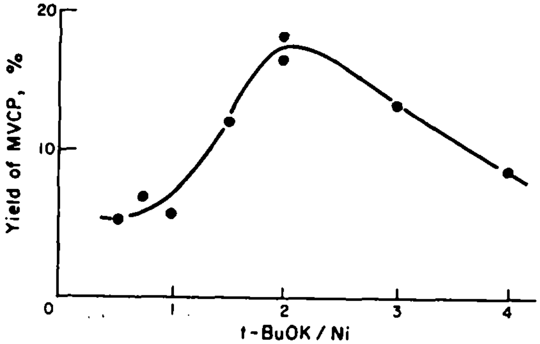
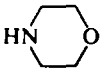
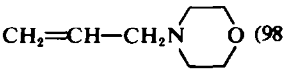
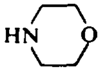
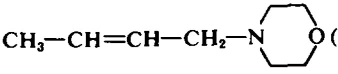
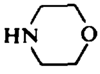
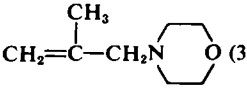
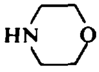
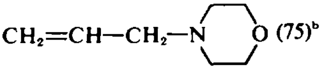
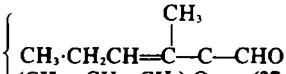


Fig 1. Effect of alkoxide on the formation of MVCP (Eq 1); $0{\cdot}6\times10^{-3}$M $(n\text{-}Bu_3P)_2Ni(NO_3)_2$ in C_2H_5OH at 80°C for 24 hr.

Table 1. Reactions of allylic compounds

Allyl compound (mmol)	YH (mmol)	Catalyst[a]	Temp. (°C)	Product (Yield, %)
$CH_2{=}CH{-}CH_2OH$ (18)	 (18)	A	80	 (98)
$CH_3{-}CH{=}CH{-}CH_2OH$ (15)	 (15)	A	80	 (58)
$CH_2{=}C(CH_3)_2{-}CH_2OH$ (15)	 (15)	A	80	 (37)
$(CH_2{=}CH{-}CH_2)_2O$ (12)	 (12)	A	80	 (75)[b]
$CH_2{=}CH{-}CH_2{-}OH$ (12)	$CH_3(CH_2)_7SH$	A	80	$CH_2{=}CH{-}CH_2{-}S{-}(CH_2)_7{-}CH_3$ (< 10)
$CH_2{=}CH{-}CH_2{\cdot}OH$ (23)	—	B	80	 $CH_3{\cdot}CH_2CH{=}\overset{\overset{\displaystyle CH_3}{\vert}}{C}{-}C{-}CHO$ (15·2) $(CH_2{=}CH{-}CH_2)_2O$ (37·1)
$CH_2{=}CH{-}CH_2OH$ (23)	—	B	40	$(CH_2{=}CH{-}CH_2)_2O$ (89·3)

[a] A, $(n\text{-}Bu_3P)_2NiBr_2$: t-BuOK = 0·3 : 0·3 (mmol). B, $Ni(Acac)_2$: $n\text{-}Bu_3P$: $NaBH_4$ = 0·3 : 0·9 : 0·15.

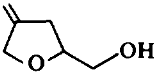
[b] Yield based on one allyl group.

methylamine or diethylamine was used, the substitution reaction with amine was no longer observed but polymeric products of the allyl compound were obtained.

In this reaction sodium borohydride and alkoxide were effective as the reducing agents of the nickel salts. When alkoxide was used, the optimum ratio of alkoxide to Ni was also around 2:1. This fact shows that zero-valent nickel is effective for this reaction. In some amines $(n\text{-}Bu_3P)_2NiBr_2$ itself showed the catalytic activity. In this case the nickel complex is presumably reduced by amine to give the active species.

Allyl alcohol is known to be isomerized to propionaldehyde via 1,3-hydrogen shift[9] or to be converted to diallyl ether[10] or to furfuryl alcohols (**1** and **2**).[11] When allyl alcohol was treated with $(n\text{-}Bu_3P)_2NiBr_2$–$NaBH_4$, 2-methyl-2-pentenal (**3**) was mainly obtained, which was formed by the aldol condensation of propionaldehyde, followed by dehydration.

On the other hand, $Ni(Acac)_2$–$(n\text{-}Bu_3P)_2$–$NaBH_4$ (1 : 2 : 0·5) gave diallyl ether. This reaction proceeds smoothly between 40 and 50°C. Higher temperature favors the isomerization to propionaldehyde (Table 1). In this reaction the presence of a controlled amount of phosphine is necessary as an auxiliary ligand. Addition of more phosphine hindered the formation of diallyl ether. Only nickel acetylacetonate was effective for this reaction. Other nickel complexes caused the isomerization of allyl alcohol. The isomerization of allylic alcohols to aldehydes or ketones by transition metal is confirmed to proceed through the transfer of one hydrogen on the α-carbon atom to the γ-position(1,3-shift).[12] However, in the etherification the first step is considered to be the formation of π-allyl complex. This is a marked difference between these two reactions.



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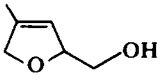

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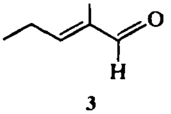

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From the present study it can not be concluded what affects strongly the course of the reactions, because transition metal-catalyzed reaction is delicately influenced by the whole ligands.

EXPERIMENTAL

Commercially available nickel acetylacetonate, nickel bromide, tri-n-butylphosphine and allylic compounds were used without further purification. 2,7-Octadienyl ethers were synthesized in a glass tube from liquefied butadiene (20 ml) and alcohol (30 ml) using $(n\text{-}Bu_3P)_2NiBr_2$ (2 mmol) and t-BuOK (6 mmol) as the catalyst. The reaction at 20°C for 48 hr gave isopropyl and ethyl ethers in 40 and 30% yields, respectively.

General procedure for the reaction was similar to that for the dimerization of butadiene reported earlier.[3] In a glass tube, nickel complex (and phosphine), sodium borohydride (or potassium alkoxide), solvent, and allylic compounds were added in this order under nitrogen atmosphere, and then the tube was sealed with a flame. After the reaction the yields of the products were determined gas-chromatographically, using an internal standard. The identification of the products was performed by comparing the retention times and, if necessary, the IR- and NMR-spectra with those of the authentic sample after separation by gas chromatography.

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