

Allylic Alcohols as Synthons of Allylic Carbanions. Palladium-Catalyzed Carbonyl Allylation by Allylic Alcohols with SnCl₂

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The tin(II) compound SnX₂ is an attractive synthetic reagent because (1) it has reducing ability and (2) it can form various coordination states.¹ The reducing ability of SnX₂ has been applied to the conversions of allylic halides or phosphates into synthons of allylic carbanions.^{2,3} The important developments in these conversions have extended the utility of the carbonyl allylation in organic syntheses. We have recently reported that catalyst PdCl₂(PhCN)₂-SnCl₂ is one of the more effective reducing systems to permit allylic acetates function as synthons of allylic carbanions in the carbonyl allylation.⁴ The functionalization results from an apparent charge reversal of the π-allylpalladium complex derived from allylic ester and Pd(0). This result has found applications of palladium catalysis in organic syntheses.^{3,5} However, the application of allylic alcohols instead of allylic esters to the charge reversal of the π-allylpalladium complex has been hitherto unknown. Here we report the carbonyl allylation by allylic alcohols via the formation and the apparent charge reversal of the π-allylpalladium complex using the catalyst PdCl₂-(PhCN)₂-SnCl₂ system.

Palladium-catalyzed allylation of carbonyl compounds by allylic alcohols with SnCl₂ proceeded at 25 °C in 1,3-dimethyl-imidazolidinone (DMI) to give homoallylic alcohols (Scheme I).⁶ Some representative results are summarized in Table I. The molar amount of SnCl₂ must be at least twice that of allyl alcohol in this carbonyl allylation (entries 1-3). Allyl alcohol, in contrast to the allyl acetate, could be used for the allylation of ketones at 50 °C (entries 9 and 10). The allylation of the aldehyde was chemoselectively performed in the presence of a ketone group (entries 11 and 12).

In the cases of 1- or 3-substituted allyl alcohols (entries 13-20), benzaldehyde regioselectively attacked the more substituted allylic position of the π-allylpalladium complex to give a single regioisomer; its stereochemistry was anti-rich except in the case of the (Z)-crotyl alcohol (entry 15).⁸ The syn-π-allylpalladium complex, which has been prepared from both (E)-crotyl and 1-methylallyl alcohol with Pd(0) and SnCl₂, has apparently caused reductive

Scheme I

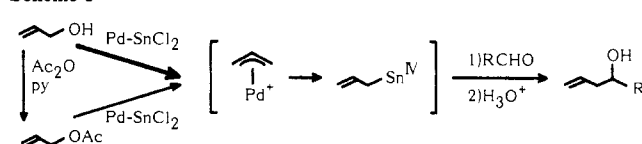


Table I. Carbonyl Allylation by Allylic Alcohols with Pd-SnCl₂^a

entry	allylic alcohol	carbonyl compd.	time (h)	product	yield ^b (%)
1		PhCHO	25-50		24 ^c
2		PhCHO	25		57 ^d
3		PhCHO	25(54) ^e		74(72) ^e
4			39		88
5		Ph-CH=CH-CHO	24		81
6		CH ₃ -CH=CH-CHO	41		62
7		CH ₃ -CH=CH-CHO	39		65
8		CH ₃ -CH=CH-CHO	26		36
9		Ph-C(=O)-Me	45		59 ^f
10			55		66 ^f
11		PhCHO : PhCOMe 1 : 1	25		72 ^h
12			29		65
13		PhCHO	36		63
14		PhCHO	7		65 ^f
15		PhCHO	47		67
16		PhCHO	24		75
17		PhCHO	73		79
18		PhCHO	89		83 ^k
19		PhCHO	65		85 ^k
20		PhCHO	50		57 ^l

^a The allylation of carbonyl compounds (1 mmol) by allylic alcohols (1.5-3 mmol) with PdCl₂(PhCN)₂ (0.02 mmol) and SnCl₂ (3 mmol) was carried out at 25 °C in DMI (3 mL). ^b Isolated yield based on the carbonyl compound. ^c Allyl alcohol:PhCHO:SnCl₂ = 1:1:1. ^d Allyl alcohol:PhCHO:SnCl₂ = 1:1:2. ^e THF as a solvent was used. ^f The reaction was carried out at 50 °C. ^g See ref 7. ^h More than 80% of acetophenone was recovered. ⁱ See ref 3. ^j See ref 9. ^k Alcohol:PhCHO:SnCl₂ = 1:2:3. ^l Alcohol:PhCHO:SnCl₂ = 1:2:2.

elimination to produce a (E)-crotyltin intermediate, which has attacked benzaldehyde at the γ-position. The anti selectivity can be explained by a chair form of the six-membered cyclic transition state. The minor syn addition seems to be based on an acyclic transition state, since coordination of DMI instead of benzaldehyde to Sn(IV) prevents the formation of the six-membered cyclic transition state. Its formation should be influenced by the reaction temperature (entries 13 and 14).¹⁰ The addition of (Z)-crotyltin compound has exhibited syn selectivity in both transition states. However, the ratio of syn vs anti was 66:34 (entry 15). The anti

(10) The diastereoselectivity in the addition of (E)-crotyl acetate was further influenced by the reaction temperature: anti selectivity at 25 °C (90 h, 61%, syn:anti = 43:57, unpublished result) and syn selectivity at 60 °C (20 h, 69%, syn:anti = 61:39, ref 4).

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addition presumably occurred via the isomerization of the *anti*- π -allylpalladium complex to the *syn* complex.

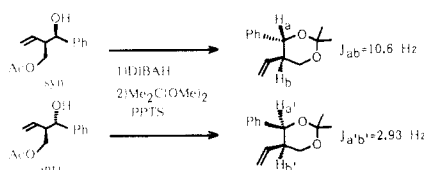
Allylic alcohols bearing either an aliphatic or an aromatic bromide chemoselectively reacted with benzaldehyde to give the corresponding homoallylic alcohols (entries 18 and 19). Under these conditions, oxidative addition of an allyl alcohol to Pd(0) proved to be faster than that of an aryl bromide.¹¹

The chemoselectivity between an allylic alcohol and an allylic acetate was investigated with 4-acetoxy-2-(*Z*)-butenol. The result demonstrated the high reactivity of allylic alcohol (entry 20). The product (X:OAc) was the same as that found in the addition of 1,4-diacetoxy-2-(*Z*)-butene (61%, *syn/anti* = 28/72). 2-(*Z*)-Butene-1,4-diol also added to benzaldehyde to produce the homoallyl alcohol (X:OH, 60%, *syn/anti* = 35/65). The addition of these 2-(*Z*)-butenes exhibited *anti* selectivity different from that of (*Z*)-crotyl alcohol.¹²

We expect that this carbonyl allylation will become a method of considerable synthetic utility, complementing the known allylmethyl method,^{8,13} since the starting allylating agents, allylic alcohols, are easily prepared and are relatively stable.¹⁴ Further studies clarifying the full scope, limitations, and mechanism of this new process are in progress.

(11) This was also true for the oxidative addition of an allyl acetate. See ref 5d.

(12) The *anti* selectivity should be dependent on the isomerization of *anti*- π -allylpalladium complex to *syn* complex easily occurring by steric hindrance of bulky substituents (X). The adduct was converted to 1,3-dioxane derivative, and the configuration was determined by following the reported results: Koga, K.; Yamada, S. *Chem. Pharm. Bull.* 1972, 20, 526.



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Chair and Boat Transition States for the Cope Rearrangement. A CASSCF Study

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Although there is general agreement that the chair Cope rearrangement of 1,5-hexadiene passes through a species with C_{2h} symmetry,² the geometry and nature of this species remain controversial. Both MINDO/2³ and MINDO/3⁴ calculations found this species to be an intermediate, with bond lengths, *R*, between the two allyl fragments of about 1.61 Å. More recent AM1 calculations gave a geometry for the non- C_{2h} transition state that was very close to that of the C_{2h} intermediate,⁵ suggesting the the Cope rearrangement might be a concerted reaction and that the

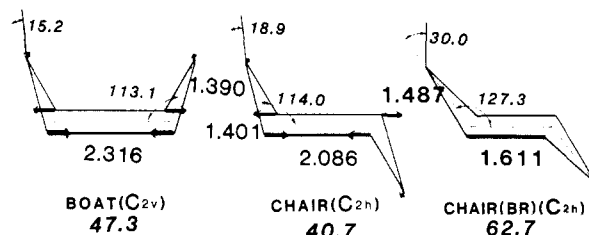


Figure 1. CAS-optimized geometries (in Å and deg) and relative energies (in kcal/mol) of boat (C_{2v}) and chair (C_{2h}) transition states and biradicaloid (BR) chair (C_{2h}) intermediate. Arrows on the transition states are the reaction coordinate.

C_{2h} species might be a transition state. Nevertheless, the value of $R = 1.646$ Å in the C_{2h} species is still indicative of a non-synchronous reaction,⁶ with bond making preceding substantial bond breaking.

In multi-bond reactions, it is essential to correlate properly all the electrons involved. Previously, we reported the results of *ab initio* 3-21G MCSCF calculations on the chair Cope rearrangement.⁷ Of the 52 1A_g configurations that arise in C_{2h} symmetry from 6 electrons in 6 active orbitals, the 12 most important configurations were used to define MCSCF orbitals for use in CI calculations which included all 52 configurations. These calculations found the C_{2h} species to be the transition state, with a much longer interallylic bond length ($R = 2.062$ Å) than those obtained by the semiempirical calculations. The bond lengths in the transition state indicated that σ bond breaking is synchronous with σ bond making in the chair Cope rearrangement.

However, these *ab initio* calculations have been criticized⁵ for their lack of full geometry optimization and incomplete vibrational analysis and for their use of an incomplete set of MCSCF configurations. Herein we report the results of MCSCF calculations on both the chair and boat Cope rearrangements that are without any of these deficiencies.

All of the calculations were performed with a complete active space (CAS) SCF wave function, consisting of all the singlet configurations that arise from the 6 electrons, which are involved in the Cope rearrangement, being distributed among 6 active orbitals. Both chair (C_{2h}) and boat (C_{2v}) geometries were fully optimized with analytical gradients,⁸ using the 3-21G basis set.⁹ The optimized geometries are shown in Figure 1. Each was characterized as a transition state by a full vibrational analysis with the Cartesian finite difference of gradients. The interallylic bond length of $R = 2.086$ Å for the chair is very similar to 2.062 Å found previously.⁷ A natural orbital analysis of the CASSCF wave functions showed that the number of electrons in the three "antibonding" MOs is 0.285 for the chair and 0.357 for the boat transition states. These antibonding orbital occupation numbers should be compared with 0.204 for 1,5-hexadiene. The transition states thus have 10-15% more diradical character than the reactant, but the transition states are still very much closed-shell species. This is indicative of the synchronous nature of the reaction.

A geometry optimization, starting from the UHF triplet geometry for the chair, converged to a second C_{2h} stationary point, which is shown as chair (BR) in Figure 1. A calculation with one interallylic CC bond stretched and the other shortened gives a higher energy, confirming that this is a local minimum, i.e., an intermediate. This species has a very short interallylic bond length, *R*, of 1.611 Å and a high "antibonding" natural MO occupation of 0.582, both of which are indicative of its biradical character. However, the energy of the biradicaloid is 22.7 kcal/mol higher than that of the $R = 2.086$ Å chair transition state and exceeds

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