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REDUCTION OF SOME POLYHALOGENATO- AND POLYACETOXY-ALLYLIC COMPOUNDS WITH TRIBUTYLTIN HYDRIDE IN THE PRESENCE OR ABSENCE OF A PALLADIUM CATALYST

I. REDUCTION OF DICHLORO- AND DIACETOXY-PROPENES

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Summary

Radical-promoted tributyltin hydride reduction of 3,3-dichloropropene, (*Z*)-1,3-dichloropropene, or (*E*)-1,3-dichloropropene yields a mixture of the three possible regio-stereoisomeric monochloropropenes. The palladium-catalyzed reduction yields regiospecifically the two stereoisomeric 1-chloropropenes with a *Z*/*E* ratio which remains constant whatever the starting dichloropropene but which is not the thermodynamic ratio. The results are against a radical mechanism and strongly support a polar π-allyl mechanism for the catalytic reactions.

Introduction

In the past few years, we [1–3] and others [4–6] have shown that the reducing properties of tributyltin hydride towards certain substrates, namely acyl chlorides [1], allylic carboxylates or halides [1–4,6], and electron-poor unsaturated compounds such as α,β-unsaturated aldehydes, ketones, and nitriles [1,3,5,6], are considerably enhanced by the presence of catalytic amounts of soluble palladium complexes. Several observations, including that of the regiospecific palladium-catalyzed hydrostannation of acrylonitrile to α-tributylstannyl propionitrile [3] and the chemospecific reduction of citronelloyl chloride to citronellal [1] without competitive formation of cyclic ketones [7–9], led us to suggest a polar rather than a radical mechanism for these catalytic processes [3].

For the catalytic reduction (hydrostannolysis) of allylic compounds, we also proposed, but did not substantiate, a polar mechanism involving a π-allyl palladium complex as the reactive electrophilic species [2]. To test this hypothesis we began a comparative study of the tributyltin hydride reduction of some polyhalogenato and polyacyloxy allylic compounds under both radical-initiated and catalytic conditions.

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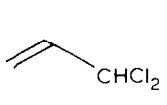
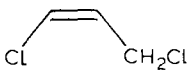
As a first step we investigated the reduction of the isomeric 3,3-dichloropropene (**1**). (*Z*)-1,3-dichloropropene (**2**) and (*E*)-1,3-dichloropropene (**3**), since significant differences in the regiochemical and stereochemical outcome of these reactions would be expected if π-allyl complex formation was effectively involved in the catalytic process. We also studied the reduction of 3,3-diacetoxypropene (**4**), but in this case only under catalytic conditions. The results of these investigations are presented here.



(**1**)



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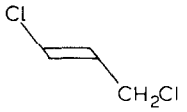
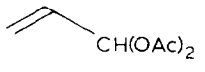
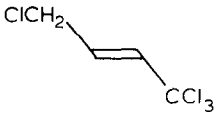


(**3**)



(**4**)

In a subsequent investigation we examined the catalytic and radical tributyltin hydride reductions of 1,1,1,4-tetrachloro-but-2-ene (**5**), and the results are presented in an accompanying paper [29].

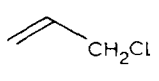


(**5**)

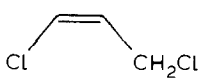
Results

Radical-initiated reduction of 3,3-dichloropropene and (Z)- and (E)-1,3-dichloropropene

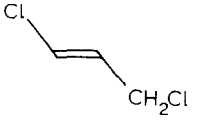
Radical reductions of compounds **1**–**3** were carried out in sealed tubes at 105°C and without solvent in the presence of azo-bisisobutyronitrile (AIBN) as initiator. In all cases, extensive decomposition of tributyltin hydride generated hexabutyldistannane and hydrogen, and up to 80% of the starting dichloride was recovered at the end of the reaction. We thus were able to confirm that no isomerization between **1**, **2** and **3** occurred under the conditions employed. The three possible monoreduction products allyl chloride (**6**), (*Z*)-1-chloropropene (**7**) and (*E*)-1-chloropropene (**8**) were obtained whatever the starting dichloropropene. In all cases, **7** was the major component (Table 1).



(**6**)

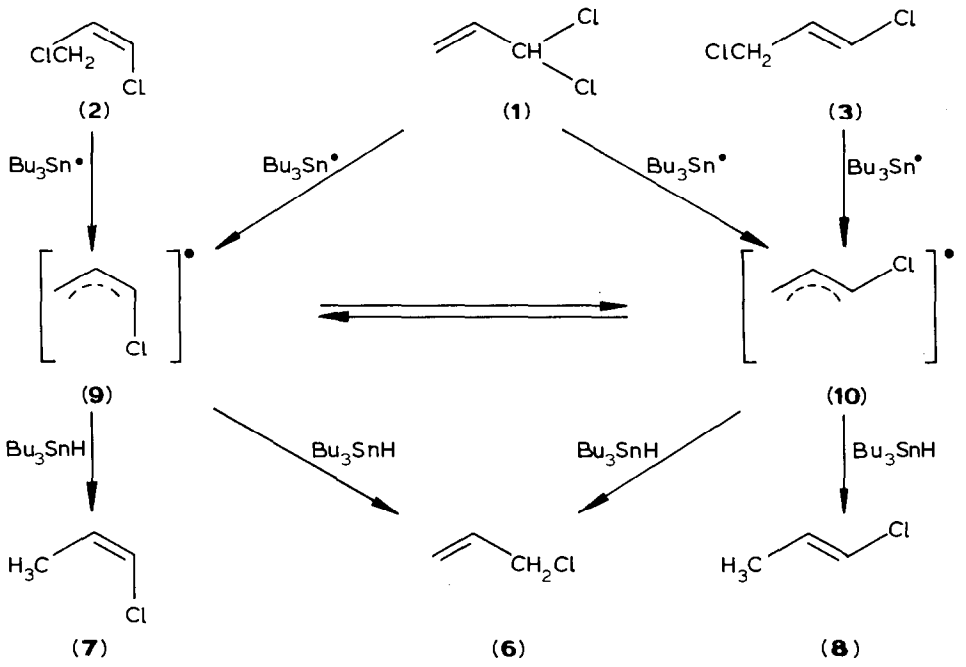


(**7**)



(**8**)

These results are readily accounted for in terms of a radical mechanism [10]. The first step in these reductions must be the formation of the two stereoisomeric allylic radicals **9** and **10**, which involves chlorine abstraction from the allylic position of **1**, **2** or **3** (Scheme 1). Tributyltin hydride then transfers a hydrogen atom to either end of the mesomeric system **9** or **10** to give either allyl chloride **6** or (*Z*)- and (*E*)-1-chloropropene **7** and **8**. The fact that (*Z*)-1-chloropropene (**7**) always predominates over the *E*-isomer seems to indicate that the two allyl radical inter-



SCHEME 1

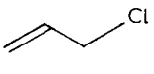
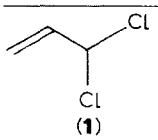
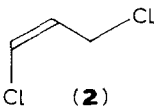
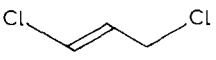
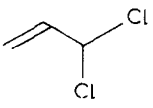
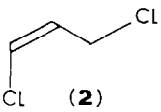
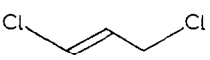
mediates may undergo configurational equilibration under the reaction conditions. A possible equilibration between **7** and **8**, for example through addition-elimination of tributyltin radical to the double bond [11] (a feature which we did not try to confirm) would not be sufficient to account for the observed stereochemistry since the Z/E ratio is always greater than the equilibrium value of 75/25 [12]. A more complete study of tin hydrides reduction involving other mesomeric radicals has been described by Menapace and Kuivila [10].

Catalytic reduction of 3,3-dichloropropene and (Z)- and (E)-1,3-dichloropropene

The palladium-catalyzed reductions of compounds **1–3** were carried out in THF at room temperature. Tributyltin hydride (1 equiv.) was added dropwise during a few minutes to a solution containing the starting dichloride (1–3 equiv.) and tetrakis(triphenylphosphine)palladium(0) ($2–6 \times 10^{-2}$ equiv.). The reactions were slightly exothermic and virtually instantaneous. The yields of reduction products, based on the amount of tributyltin hydride used, were found to be quantitative (> 90%) within experimental error in all cases. Complete regioselectivity towards the formation of (*Z*)- (**7**) and (*E*)-chloropropene (**8**) was observed. No allyl chloride was detected even when a large excess (two- to three-fold) of dichloropropene relative to tributyltin hydride was used. In a competition experiment in which one equivalent of 3,3-dichloropropene and one equivalent of allyl chloride were allowed to react catalytically with one equivalent of tributyltin hydride, both compounds were reduced to comparable extents. The absence of allyl chloride in the palladium-catalyzed reduction of dichloropropene thus cannot be the result of its further (very fast) reduction to propene under catalytic conditions. As for the stereochemistry of the reactions, the **7**/**8** ratio (Z/E ratio for 1-chloropropene) was found to be almost

TABLE 1

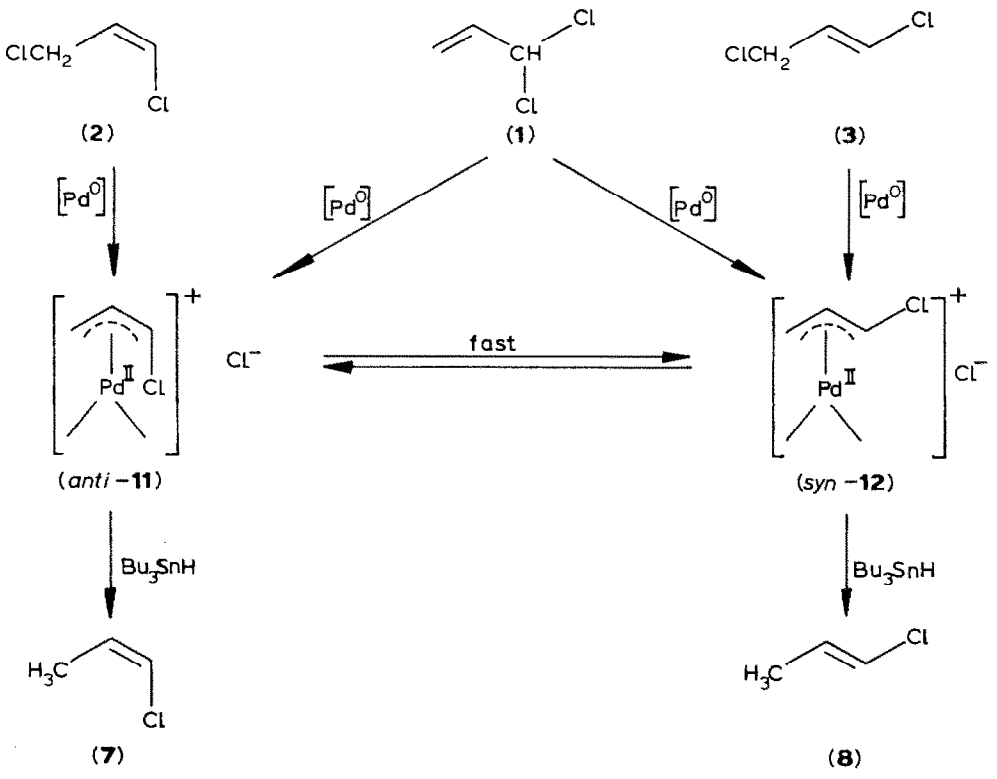
RADICAL- AND PALLADIUM-CATALYZED TRIBUTYLTIN HYDRIDE REDUCTION OF DICHLOROPROPENES

Starting material	Method [a]	Product (%)			7/8 (Z/E)
		 (6)	 (7)	 (8)	
 (1)	A	12	73	15	83/17
 (2)	A	15	72	13	85/15
 (3)	A	10	71	19	79/21
 (1)	B	0	38	62	38/62
 (2)	B	0	35	65	35/65
 (3)	B	0	36	64	36/64

[a] A: AIBN initiated, 105°C, 1 h. B: Palladium-catalyzed, THF, room temperature.

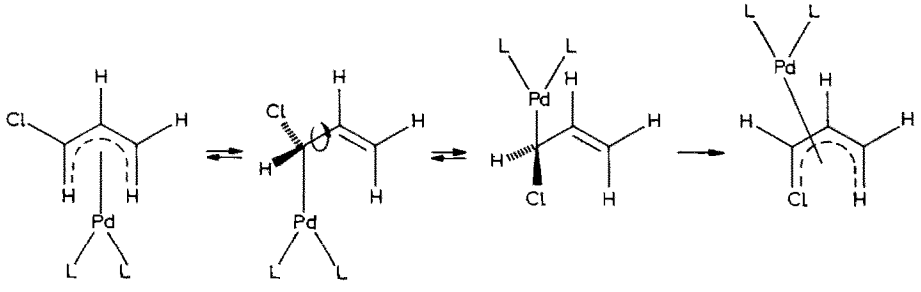
constant (around 35/65) for all three catalytic reductions (Table 1).

The regiochemical and stereochemical outcome of the palladium-catalyzed hydrostannolysis of compounds **1**–**3** thus appears to be in sharp contrast to those of the radical reactions. We also established that tetrakis(triphenylphosphine)palladium(0) does not catalyze any isomerization between **1**, **2** and **3** or between **6**, **7** and **8**, and so the catalytic reductions are undoubtedly under kinetic control. The fact that the distribution of the reduction products from **1**, **2** or **3** being the same implies that a common intermediate is involved whatever the starting dichloropropene. From what is known about the palladium-catalyzed allylation of nucleophiles [13], this intermediate is very likely to be an allyl complex of the metal.



SCHEME 2

The following mechanism is proposed to account for the results described (Scheme 2). In a first irreversible step, (since palladium does not promote equilibration of the starting dichloropropenes) **2** and **3** react with the palladium(0) complex to give the *anti*-**11** [14] and the *syn*-**12** [14] π-allyl complexes. Reaction of 3,3-dichloropropene **1** leads to either **11** or **12** depending on which stereotopic chlorine substituent is displaced by palladium. The fact that the Z/E ratio is the same for all



12 (π) (σ) (σ) **11** (π)

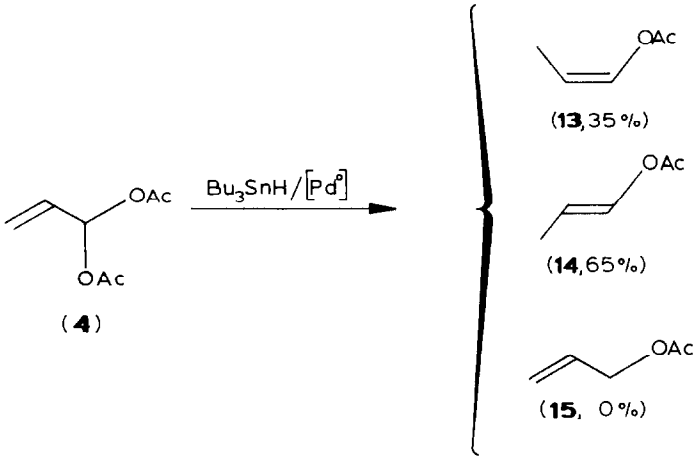
(L = PPh_3)

SCHEME 3

reactions shows that the *syn* and *anti* complex **11** and **12** rapidly equilibrate, probably through a $\pi-\sigma-\pi$ mechanism (Scheme 3) [15]. The high (non-thermodynamic [12]) E/Z ratio for 1-chloropropene indicates that the transition state leading to (*E*)-1-chloropropene is lower in energy than that leading to (*Z*)-1-chloropropene (Curtin–Hammond principle). This, in turn, probably reflects the greater stability of the *syn*-**12** over the *anti*-**11** π-allyl complex. The irreversibility of the π-allyl complex formation, the rapid equilibration between the *syn* and *anti* stereoisomers, and the (probable) greater stability of the former over the latter are in line with a recent exhaustive study by Bosnich and coworkers [15,16] of asymmetric catalytic allylic alkylation.

Catalytic reduction of 3,3-diacetoxypropene

The catalytic reduction of 3,3-diacetoxypropene gave results similar to the ones obtained in the reduction of dichloropropenes. The two stereoisomeric (*Z*)-**13** and (*E*)-**14** propanal enol acetates were selectively and quantitatively obtained, in 35/65 ratio. No allyl acetate **15** could be detected in the medium.

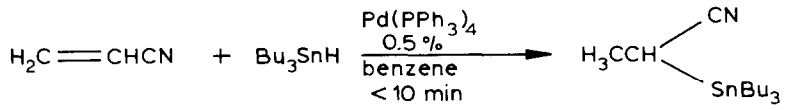


A mechanism similar to that depicted in Scheme 2 but involving 1-acetoxy π-allyl complexes can account for the results.

Discussion

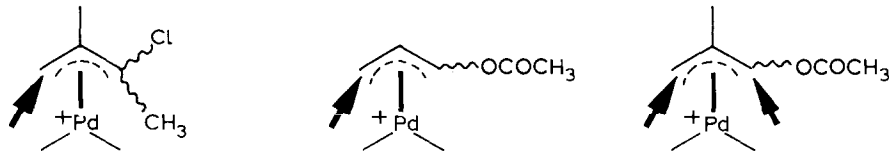
The results strongly support the proposal that π-allyl metal complexes are formed as reactive intermediates in the palladium-catalyzed tributyltin hydride reduction of dichloro- and diacetoxypropene and thus, by extension, of allylic halides and carboxylates in general. π-Allyl complexes are not, however, extremely powerful electrophiles; e.g. they do not react with weak nucleophiles such as the anion of Meldrum's acid [17]. Tin hydrides, on the other hand are very poor nucleophiles. Some activation of the nucleophilic properties of tributyltin hydride [1,3,4] concomitant with the formation of π-allyl complex, is thus needed to account for the rapidity of the catalytic allylic reduction. A similar conclusion can also be drawn from the marked rate enhancements brought about by palladium catalysts in the hydrostannation of electron-poor olefins [3]; e.g. the palladium-catalyzed hydro-

stannation of acrylonitrile (**16**) to α-tributylstannyl propionitrile (**17**) is extremely fast at room temperature whereas the corresponding polar non-catalytic reaction requires drastic conditions (150°C, several hours) [18]. The regiospecificity of the catalytic reaction leading to **17**, to the exclusion of β-tributylstannyl propionitrile, also points to a polar mechanism [18]. The activation of hydride donor properties of tributyltin hydride probably occurs via an oxidation addition process to form a palladium hydride species as in the reaction of triphenyltin hydride with hydridocarbonylbis(triphenylphosphine)iridium(I) [19].



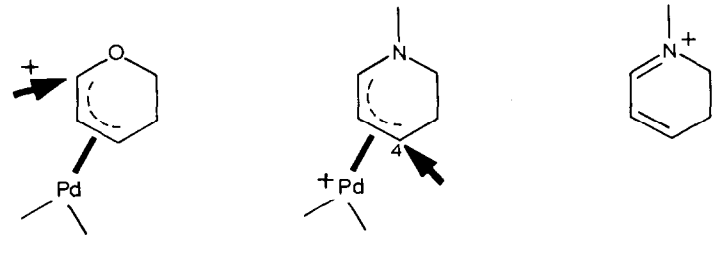
(**16**) (**17**)

Coming back to the catalytic reduction of dichloro and diacetoxy propenes, the reasons for the regiospecific character of hydride attack on the intermediate 1-acetoxy- and 1-chloro π-allyl- palladium complexes are rather obscure. The literature reports on related reactions are rather confusing. The palladium-catalyzed condensation of potassium enoxyborates with 1,3-dichloro-2-methyl-but-2-ene, which must involve **18** as the reactive intermediate, occurs regiospecifically at the carbon distal to the chlorine substituent [20]. Similarly, Trost and coworkers observed a bias towards attack at the carbon distal to the oxygen atom in the condensation of 3,3-diacetoxypropene (presumed intermediate **19**) with α-methyl dimethyl sodiomalonate [21]. However a reverse selectivity is observed in the condensation of **20** with the less sterically congested dimethylsodiomalonate [21].



(**18**) (**19**) (**20**)

Selectivity towards attack at the carbon proximal to the oxygen atom is also observed in the condensation of dehydropyranyl acetate (presumed intermediate **21**) with diethyl sodioformamido malonate [22]. Finally, the palladium-promoted condensation of 2-cyano-3-piperidine with dimethylsodiomalonate occurs selectively at C(4) but the question of whether the electrophilic species in the medium is the palladium complex **22** or the dihydrido pyridinium cation **23** freed from palladium has not been elucidated [23].



(**21**) (**22**) (**23**)

Clearly the directing effect of an heteroatomic substituent X (X = Hal, OR, OCOR, NR_2) in the electrophilic condensations of X-substituted π-allyl complexes is difficult to rationalize at the present time, and may depend on a complex array of steric, stereochemical and electronic factors.

Experimental

Measurement

The instruments used were: (i) for IR, Perkin–Elmer Model 457; for ^{1}H NMR, Perkin–Elmer Model R 12 (90 MHz); for GLC, Carlo Erba Fractovap 2150 Model equipped with a 5 m × 2 mm 3% OV 225 column (column A); Capillary GC: Carlo Erba Fractovap 4130 Model equipped with a SE 54 coated 15 m glass capillary column.

Materials and references compounds

THF was distilled from sodium benzophenone. Tributyltin hydride was prepared from polymethylhydrogenosiloxane (PMHS) (Fluka) and bis(tributyltin) oxide [24]. $Pd(PPh_3)_4$ was prepared as previously described [1].

A mixture of the dichloropropene **1**, **2** and **3** was prepared from phosphorus pentachloride and acrolein [25]. Pure isomers were obtained by fractional distillation with spinning band column. A commercial sample (Janssen) was also found to be pure (> 97%) (*Z*)-1,3-dichloropropene. 3,3-Diacetoxypropene was prepared from acrolein according to the recent procedure [26] of Pinnick and coworkers (Ac_2O, $FeCl_3$).

^{1}H NMR spectra (90 MHz $CDCl_3$), δ (ppm): 3,3-dichloropropene (**1**): 5.0–5.4 (m, 2H, terminal vinylic H), 5.8–6.2 (m, 2H, allylic and internal vinylic H); (*E*)-1,3-dichloropropene (**3**): 4.02 (d, *J* 7 Hz, 2H), 5.9–6.45 (2H, m); (*Z*)-1,3-dichloropropene (**2**): 4.20 (br. d, *J* 7.5 Hz, 2H, allylic H), 6.0 (q, $J_1 = J_2 = 7.5$ Hz, 1H, vinylic H(2)), 6.23 (br d, *J* 7.5 Hz, 1H, vinylic H(1)).

(*Z*)-**7** and (*E*)-1-chloropropene **8** were respectively prepared by $LiAlH_4$ reduction [27] of (*Z*)-1,3-dichloropropene and (*E*)-1,3-dichloropropene. (*Z*)- and (*E*)-1-acetoxypropene **13** and **14** were prepared from propanal as described by House [28].

^{1}H NMR spectra (90 MHz, $CDCl_3$), δ (ppm): (*E*)-1-chloropropene (**8**): 1.68 (d, *J* 6 Hz, 3H), 5.65–7.05 (m, 2H); (*Z*)-1-chloropropene (**7**): 1.75 (d, *J* 6 Hz, 2H), 5.61 (br. quintet, $J_1 \simeq J_2 \simeq 6$–7 Hz, 1H, vinylic H(2)), 6.05 (v. br. d., $J \simeq 7$ Hz, 1H, vinylic H(1)); (*Z*) and (*E*)-1-acetoxypropene: ref. 28.

Tributyltin hydride reduction of dichloro- and diacetoxy-propene

Radical reductions were carried out in tubes sealed under vacuum using 1 equiv. of tributyltin hydride. 1 equiv. of the starting dichloropropene, and 1.6×10^{-2} equiv. of azobisisobutyronitrile. After 1 h at 105°C in an oil bath the tube was cooled in an ice bath and opened, and the mixture was analyzed by GLC after dilution in THF.

Catalytic reductions were performed under argon as follows. To a THF solution (1–2 ml) of the organic substrate (1–3 mmol) and of the catalyst ($Pd(PPh_3)_4$, 0.02–0.06 mmol) tributyltin hydride (1 mmol) was added dropwise with stirring from a syringe during about 1 min. After stirring for a further 10 min, the reaction mixture was analyzed by GLC. GLC analyses were performed on column A (see

above) with temperature programming: T 15°C for 13 min, then 15–100°C during 1 h. Products were eluted in the following order: (Z)-1-chloropropene, (E)-1-chloropropene, allylchloride, THF, 3,3-dichloropropene, and (Z)-1,3-dichloropropene. The amount of each compound was determined from the peak area. The system was calibrated with mixtures of authentic samples of the products, and the NMR data for these products were also available.

Acknowledgement

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