

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

II*. REDUCTION OF 1,1,1,4-TETRACHLOROBUT-2-ENE

F. GUIBÉ*, YANG TING XIAN and G. BALAVOINE

*Laboratoire de Chimie Organique des Eléments de Transition UA-CNRS No. 255, Institut de Chimie
 Moléculaire d'Orsay, Bât. 420 91405 Orsay Cedex (France)*

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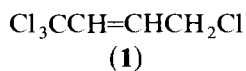
Summary

The radical tributyltin hydride reduction of 1,1,1,4-tetrachlorobut-2-ene yields a mixture of the expected 1,1,4-trichlorobut-2-ene and 1,1,4-trichlorobut-1-ene resulting from preferential abstraction of a chlorine atom from the trichloromethyl group. The palladium-catalyzed reduction follows an entirely different course, giving 1,1-dichlorobutadiene exclusively and quantitatively. The palladium-catalyzed reaction involves an oxidative addition- β -elimination process leading to dichlorobutadiene and a dichloropalladium(II) species. Tributyltin hydride reduction of palladium(II) to palladium(0) completes the catalytic cycle.

Introduction

In the preceding paper [9], we described a comparative study of the radical-promoted and the palladium-catalyzed tributyltin hydride reduction of isomeric dichloropropenes. We concluded that the catalytic reduction follows the general pattern [1] for palladium-catalyzed condensations of allylic electrophiles with nucleophiles, viz.: (i) formation of a π -allyl complex of the metal; (ii) condensation of this new electrophilic species with the nucleophile (a hydride species in the present case).

In this paper we discuss the radical and the palladium-catalyzed reduction of 1,1,1,4-tetrachlorobut-2-ene (**1**).



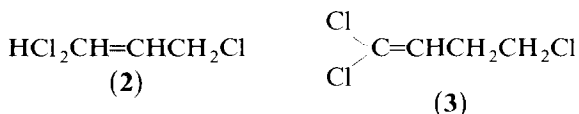
* For part I see ref. 9.

Our initial goal in this study was mainly to gain some insight of the nature of the oxidative addition process leading to π -allyl palladium complex. Indeed despite the wide interest in π -allyl metal chemistry this particular aspect of the reaction has been rather overlooked. Oxidative addition of organic halides to transition metals may in general proceed by an S_N2 -type or a radical-type process [2], depending on the nature of the metal, of the ligand, and of the electrophile. In the case of 1,1,1,4-tetrachlorobut-2-ene, in a radical or single electron transfer process the trichloromethyl group is more prone to undergo displacements [3,4] while the monochloromethyl group is a reactive electrophilic centre towards S_N2 -attack [4]. Thus the regiochemistry of the catalytic reduction should give some information about the question of whether the formation of the π -allyl palladium complex involves an S_N2 or an electron transfer process. As for the non-catalytic (radical) reduction with tributyltin hydride it was expected that the trichloromethyl group of the molecule would be preferentially involved [5]. In the event, the catalytic process was found to follow an unexpected course and the results do not provide an answer to the above question. On the other hand, the reaction observed provides a route to halosubstituted butadienes from polyhalogenato allylic compounds under very mild conditions.

Results and discussion

Radical reduction of 1,1,1,4-tetrachlorobutene

The radical reduction of **1** was carried out without solvent in the presence or absence of AIBN (Table 1). When the reaction was carried out at 80°C for 20 min, two products were obtained, 1,1,4-trichlorobut-2-ene (**2**) and 1,1,4-trichlorobut-1-ene (**3**), identified in the reaction mixture by NMR and GC/MS analysis.



The ratio of **2** to **3**, which was ca. 30/70, was found to be unaffected by the addition of AIBN. Owing to competitive decomposition of tributyltin hydride into hexabutyldistannane and hydrogen, some of the organic substrate was still present at the

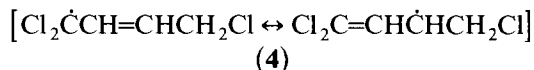
TABLE 1
RADICAL REDUCTION OF 1,1,1,4-TETRACHLORO-2-BUTENE (**1**)

Conditions			Conversion (%)	Product (rel. %)	
Initiation ^a	Temperature (°C)	Time (min)		2	3
A	80	20	64 ^b	33	67
A	80	15	50 ^b	32	68
B	80	20	28	30	70
B	80	20	29	30	70
B	15–20	1 week	95	96–98	4–2

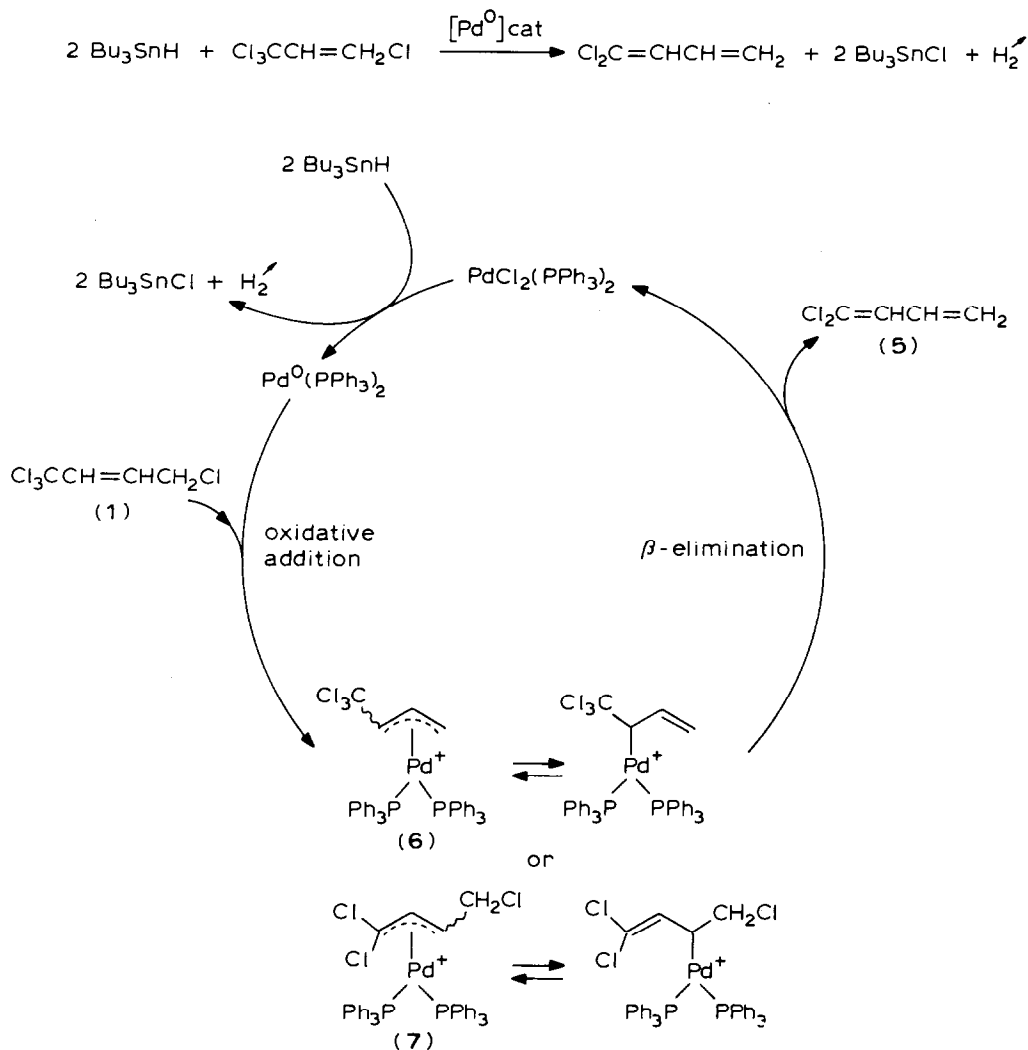
^a A: AIBN 1.6×10^{-2} equiv.. B: without radical initiator. ^b Competitive decomposition of tributyltin hydride into hexabutyldistannane and hydrogen was observed.

end of the reaction. By comparison, when the mixture of **1** and tributyltin hydride was kept for a week at room temperature under argon, 1,1,4-trichlorobut-2-ene (**3**) was formed almost exclusively and quantitatively.

The formation of the products **2** and **3** is consistent with a radical mechanism involving, as was expected, the abstraction of a chlorine atom from the trichloromethyl group. The mesomeric allylic radical **4** thus formed then reacts with tributyltin hydride to give either **2** or **3**.



The reasons for the variation of the ratio of **2** to **3** with the conditions (80°C or room temperature) used were not investigated. They are possibly related to a competition between thermodynamic and kinetic control.



SCHEME 1

Catalytic reduction of 1,1,1,4-tetrachlorobut-2-ene

Slow addition of tributyltin hydride to a solution of 1,1,1,4-tetrachlorobut-2-ene (**1**) in THF, benzene, or DMF in the presence of 5×10^{-2} equiv of dichlorobis(triphenylphosphine)palladium(II), led to a sharp change in colour from pale lemon to golden yellow. This is strongly indicative of a reduction of a palladium(II) to a palladium(0) species, and it took place after the addition of 2 equiv. of tin hydride. GC/MS analysis of the reaction mixture, after appropriate work-up, revealed a complete reduction of **1** to a single volatile product with the molecular formula $C_4H_4Cl_2$. This compound was shown by 1H NMR and ^{13}C NMR spectroscopy to be 1,1-dichlorobutadiene (**5**). The yield of **5** was essentially quantitative.

When 1 equiv. of **1** was added to a THF solution of 1 equiv. of $Pd(PPh_3)_2$ (prepared in situ by reaction of $PdCl_2(PPh_3)_2$ with 2 equiv. of tributyltin hydride) a precipitate separated immediately. The precipitate was identified, after filtration as $PdCl_2(PPh_3)_2$ (IR). GC/MS analysis of the filtrate revealed the presence of 1,1-dichlorobutadiene (**5**).

On the basis of these findings, we suggest that the tributyltin hydride palladium-catalyzed reduction of 1,1,1,4-tetrachlorobut-2-ene (**1**) to 1,1-dichlorobutadiene (**5**) (Scheme 1) involves oxidative addition of **1** to $Pd(PPh_3)_2$ to give the π -allyl complexes **6** or **7**, with **6** or **7** then undergoing a fast β -elimination of Cl^- to give dichlorobutadiene **5** and $PdCl_2(PPh_3)_2$. (The lability of a chlorine substituent next to a π -allyl function has been recognized previously [6].) Finally, reduction of $PdCl_2(PPh_3)_2$ to $Pd^0(PPh_3)_2$ by two molecules of tributyltin hydride completes the catalytic cycle.

Obviously, no indication as to which π -allyl complex **6** or **7** is preferentially formed from **1** is given by the present results. Clearly other polyhalogenato allylic compounds will have to be studied to elucidate this problem. Meanwhile, because halobutadienes are an important class of compounds, especially in polymer chemistry, the ready quantitative formation of 1,1-dichlorobutadiene from 1,1,1,4-tetrachlorobutene under the very mild conditions described here suggests that the use of the Bu_3SnH /palladium reducing system could be extended to other polyhalogenato allylic compounds to give various halosubstituted dienes. We are currently investigating these reactions from the mechanistic and synthetic points of view.

Experimental

Measurement

1H NMR spectra at 400 MHz were recorded with a Bruker AM 400 and ^{13}C NMR spectra at 250 MHz with a Bruker AM 250 at 62.9 MHz. Details of other instruments used are given in the preceding paper [9].

Materials

Benzene and DMF were purified by distillation from calcium hydride. THF was distilled from sodium benzophenone. $PdCl_2(PPh_3)_2$ was obtained by treating sodium tetrachloropalladate with 2 equiv. of triphenylphosphine in ethanol solution [7].

1,1,1,4-Tetrachlorobut-2-ene was prepared by a published procedure [8].

1,1,1,4-Tetrachlorobut-2-ene. NMR (90 MHz, $CDCl_3$), δ (ppm): 4.1–4.15 (m, 2H), 6.35–6.50 (m, 2H); IR (neat) 1625 cm^{-1} (C=C); GC/MS (70 eV) m/e (rel. intensity): 163, 161, 159, 157 (3, 28, 88, 100, $M - Cl$) 126, 124, 122 (0.6, 4.7, 6.5.

$M - 2Cl$), 125, 123, 121 (4.5, 26, 41, $M - H - 2 Cl$), 87 (30), 85 (40), 61 (12), 51 (22), 50 (16). The preparations of other materials are described in the preceding paper [9].

Radical tributyltin hydride reduction of 1,1,1,4-tetrachlorobut-2-ene

Radical reductions of 1,1,1,4-tetrachlorobut-2-ene were carried out by treating the chloro compound (1 equiv.) with tributyltin hydride (1 equiv.) in a Schlenk tube under argon. Some reactions (see Table 1) were performed in the presence of 1.6×10^{-2} equiv. of azobisisobutyronitrile. The reaction mixtures were analyzed by NMR spectroscopy after dilution with $CDCl_3$ and by GC/MS spectroscopy after dilution with pentane.

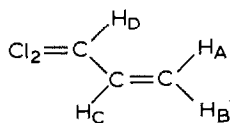
Spectroscopic data: NMR (400 MHz, $CDCl_3$), δ (ppm): $CHCl_2HC=CHCH_2Cl$: 4.07 (d, J 6 Hz, 2H), 6.16–5.98 (m, 2H), 6.21 (d, J 7.5 Hz, 1H). $CCl_2=CHCH_2CH_2Cl$: 2.65 (q, $J_1 = J_2 = 7$ Hz, 2H), 3.54 (t, J 7 Hz, 2H), 5.95 (t, J 7 Hz, 1H). IR (CCl_4): $CHCl_2CH=CHCH_2Cl$: 1665 cm^{-1} (C=C); $CCl_2=CHCH_2CH_2Cl$: 1625 cm^{-1} (C=C). GC/MS (70 eV), m/e (rel. intensity): $CHCl_2CH=CHCH_2Cl$: 162, 160, 158 (0.4, 1.6, 1.8, M^+), 127, 125, 123 (6.7, 53.5, 85.4 $M - Cl$), 113 (2.1), 111 (5.5), 109 (16.0), 87 (30), 51 (100); $CCl_2=CHCH_2CH_2Cl$: 164, 162, 160, 158 (0.4, 5.3, 26.8, 30.7, M^+), 113, 111, 109 (18.9, 70.5, 100, $M - CH_2Cl$), 87 (23), 85 (20), 51 (65).

Catalytic reduction of 1,1,1,4-tetrachlorobut-2-ene

To a suspension of $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol) in 1.5 ml of THF in a Schlenk tube under argon was added 30 μ l (ca. 0.11 mmol) of tributyltin hydride. After a few minutes, a homogeneous gold-yellow solution was obtained. 1,1,1,4-Tetrachlorobut-2-ene (196 mg, 1 mmol) was added from a syringe to the reaction mixture, to give an immediate pale yellow precipitate ($PdCl_2(PPh_3)_2$). Tributyltin hydride (600 μ l, ca. 2.2 mmol) was then slowly added from a syringe during 45 min. Towards the end of the addition the mixture once again became homogeneous and golden-yellow. The THF solution was diluted with two volumes of pentane and the organic solution repeatedly extracted (4 to 5 times) with 10% aqueous HCl to remove THF; each acid washing was re-extracted with a small volume of pentane. After further washing with neutral water the two pentane extracts were combined and dried over $MgSO_4$. After filtration, pentane was partially removed under reduced (100 mmHg) pressure. The concentrated pentane solution was analyzed by GC/MS and 90 MHz NMR spectroscopy. The yield (85–90%) was determined by NMR spectroscopy (benzene as the reference).

For better resolution, a sample free from tin compounds was obtained by bulb to bulb transfer under reduced pressure (15 mmHg) and analyzed by 1H NMR spectroscopy at 400 MHz and by ^{13}C spectroscopy.

1H NMR (400 MHz, $CDCl_3$) (ppm): assignments made after decoupling experiments:



H_A 5.37, d J_{AC} 16.5 Hz; H_B 5.28, d J_{BC} 9.5 Hz; $H_C + H_D$ 6.31–6.55, m. ^{13}C NMR (250 MHz, $CDCl_3$): 120.48, 129.36, 131.05, 122.30. GC/MS (70 eV) m/e (rel.

intensity): 126, 124, 122 (5.4, 30.0, 46.8, M^+), 89, 87 (32, 100, $M - Cl$), 51 (78), 50 (38).

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