CHEMISTRY LETTERS, pp. 1379-1382, 1982. © The Chemical Society of Japan 1982

RHODIUM(I)-CATALYZED REACTION OF 2-PROPENYL CHLOROACETATE. FORMAL ELIMINATION OF ALLENE AND INSERTION INTO THE C-O BOND OF THE ESTER FUNCTION

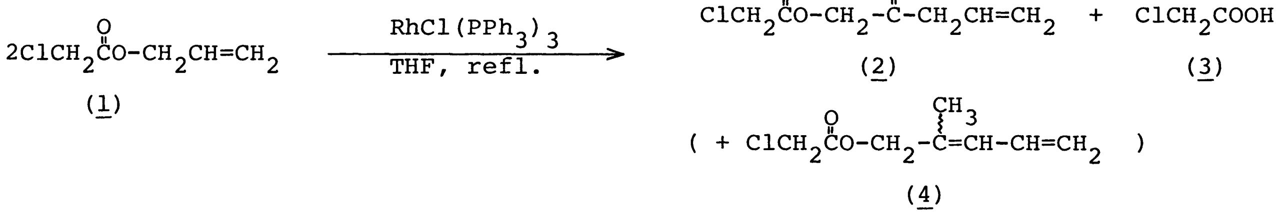
Sotaro MIYANO,* Atsuo MORI, Katsumi KATO,† Yasuhiko KAWASHIMA, and
Harukichi HASHIMOTO
Department of Applied Chemistry, Faculty of Engineering,
Tohoku University, Aramaki-Aoba, Sendai 980
†Japan Synthetic Alcohol Co., Ltd.,
10-8, Ukishima, Kawasaki-ku, Kawasaki 210

Treatment of 2-propenyl chloroacetate with catalytic amount of $RhCl(PPh_3)_3$ in boiling tetrahydrofuran gave 2-methylene-4-pentenyl chloroacetate, a product which is derived via a formal insertion of allene unit into the C-O bond of the starting chloroacetate, with concomitant formation of chloroacetic acid.

Recently, palladium-promoted C-O bond cleavage of allylic alcohol derivatives such as ethers and esters has extensively been utilized in various synthetic transformations[1]; it is generally accepted that subsequently formed π-allylpalladium intermediates play the key role in these reactions.[2] Rhodium catalysts, however, have rarely been utilized in such reactions that accompany the C-O bond fission of allylic compounds.[3,4]

We report here a rhodium(I)-catalyzed reaction of 2-propenyl chloroacetate (1) to give 2-methylene-4-pentenyl chloroacetate (2) and chloroacetic acid (3) (Scheme 1). A part of 2 was isomerized to 2-methyl-2,4-pentadienyl chloroacetate (4) under the reaction conditions.

Scheme 1.



$$\underset{(1)}{2ClCH_2\overset{O}{\overset{\|}{C}}O\text{-}CH_2CH{=}CH_2} \xrightarrow[\text{THF, refl.}]{RhCl(PPh_3)_3} \underset{(2)}{ClCH_2\overset{O}{\overset{\|}{C}}O\text{-}CH_2\text{-}\overset{CH_2}{\overset{\|}{C}}\text{-}CH_2CH{=}CH_2} + \underset{(3)}{ClCH_2COOH}$$

$$(\ +\ \underset{(4)}{ClCH_2\overset{O}{\overset{\|}{C}}O\text{-}CH_2\text{-}\overset{CH_3}{C}{=}CH\text{-}CH{=}CH_2}\ )$$

In a typical example, a solution of 1 (8.81 mmol) in THF (5 ml) in the presence of $RhCl(PPh_3)_3$ (0.143 mmol) was refluxed for 3 h under a nitrogen atmosphere. GLC analysis of the resulting reaction mixture showed the presence of 2 (1.33 mmol) and 4 (0.214 mmol) with the conversion of the substrate 1 of 52%. After the usual work-up (dilution with hexane to precipitate the catalyst, washing with aqueous 1 M $NaHCO_3$ and then water, and drying over Na_2SO_4), removal of solvents under re-

Table 1. Rhodium-Promoted Reaction of 2-Propenyl Chloroacetate[a)]

Rh-Complex	Solvent	Temp/°C	Time/h	Conversion/%	Yield/% 2	Yield/% 4
$RhCl(PPh_3)_3$	THF	66	1	37	21	3.3
	THF	66	3	52	30	4.9
	THF	66	8	59	33	6.1
	THF	Ambient	72	3.2	3.2	0
	THF[b)]	66	3	2.8	0	0
	Dioxane	101	3	71	28	4.9
	Dioxane	66	3	68	30	3.9
	Toluene	111	3	55	26	5.3
	Toluene	66	3	38	15	2.5
	Benzene	80	3	57	23	4.8
	Acetonitrile	82	3	33	7.7	0.8
$RhH(PPh_3)_4$	THF	66	3	39	16	1.5
$RhCl(CO)(PPh_3)_2$	Toluene	111	3	7.9	3.0	0
$Rh(cyclooctene)_2Cl/(dpe)_2$	Benzene	80	3	0	0	0
$RhCl_3\cdot 3H_2O$	Toluene	111	3	0	0	0

a) 1, ~9 mmol; solvent, 5 ml; 1/[Rh] ≈ 65. Conversion of 1 and yields of 2 and 4 were determined by GLC based on the 1 charged. dpe = 1,2-bis(diphenylphosphino)ethane. b) Allene was bubbled into the reaction mixture.

duced pressure followed by preparative GLC (Silicone DC-550) afforded analytical samples of 2 and 4, which were characterized by elemental analysis and spectral studies.[5)] From the aqueous washings was recovered chloroacetic acid (3).[5)]

Among the rhodium complexes examined, only $RhCl(PPh_3)_3$ and $RhH(PPh_3)_4$ showed appreciable activity for the reaction of 1 (Table 1). The reaction scarcely proceeded at ambient temperature in THF. Elongation of the reaction period in boiling THF or variation of the medium hardly improved the conversion of 1 and yields of 2 and 4. Judging from the amount of reacted 1, the turn-over number of the catalyst was estimated to be 40-45 at most. It seemed that an active catalyst species was converted into poorly active complex, $RhCl(CO)(PPh_3)_2$, at a rather early stage of the reaction[6)] (see Table 1).

Palladium- and nickel-phosphine complexes, such as $Pd(PPh_3)_4$, $Pd(dpe)_2$, $PdCl_2(PPh_3)_2$, $Ni(dpe)_2$, and $NiCl_2(PPh_3)_2$, gave no trace of 2 or 4 (THF, reflux, 3 h). In the presence of $RuCl_2(PPh_3)_3$ (2 mol%), heating of a solution of 1 in toluene at reflux for 8 h caused complete migration of the double bond to 1-propenyl chloroacetate without C-O bond fission.[7)]

Table 2 shows the $RhCl(PPh_3)_3$-promoted reaction of several allylic alcohol derivatives.[8)] 2-Propenyl dichloroacetate gave 2-methylene-4-pentenyl dichloroacetate (11).[9)] Based on the substrate consumed, the reactivity of the esters was in the order of 1>6>>5. Though 2-methyl-2-propenyl chloroacetate (8) was recovered unchanged, almost all of 2-butenyl chloroacetate (7) was cleaved into butadiene

Table 2. $RhCl(PPh_3)_3$-Promoted Reaction of Allylic Compounds[a)]

Substrate	Solvent	Conversion/%	Product(s) [Yield/%]
$CH_3COOCH_2CH=CH_2$ (5)	THF	<1	———
$CH_3COOCH_2CH=CH_2$ (5) b)	THF	58	$CH_3COOCH_2C(=CH_2)CH_2CH=CH_2$ (10) [58]
$ClCH_2COOCH_2CH=CH_2$ (1)		88	$ClCH_2COOCH_2C(=CH_2)CH_2CH=CH_2$ (2) [17]
$Cl_2CHCOOCH_2CH=CH_2$ (6)	Dioxane	36	$Cl_2CHCOOCH_2C(=CH_2)CH_2CH=CH_2$ (11) [15]
$ClCH_2COOCH_2CH=CHCH_3$ (7)	Dioxane	92	$CH_2=CH-CH=CH_2$
$ClCH_2COOCH_2C(CH_3)=CH_2$ (8)	THF	0	———
$PhOCH_2CH=CH_2$ (9)	Toluene	69	$PhOCH=CHCH_3$ (12) [69]

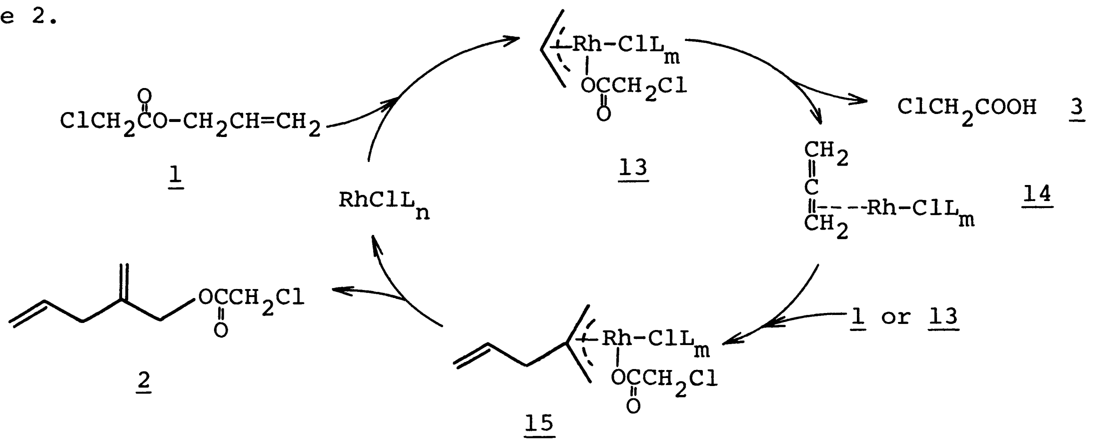
a) Substrate, ~9 mmol; [Subs]/[Rh] ≈ 65; solvent, 5 ml; reflux, 3 h. Yields were determined by GLC based on the substrate charged. b) A mixture of 5 (9 mmol) and 1 (9 mmol); [5 + 1]/[Rh] = 65; solvent, 10 ml.

and 3. Phenyl 2-propenyl ether was isomerized to 1-propenyl ether (12).[10)]

It should be noted that 2-propenyl acetate (5) did not react by itself. In the presence of 1, however, 5 gave the corresponding formal allene insertion product, 2-methylene-4-pentenyl acetate (10),[11)] in a fairly good yield. The fact that all of the reacted 5 was converted to 10 clearly shows that the allene moiety in 10 originated from 1. It is also interesting that reactivity of 1 itself was somewhat enhanced by the co-existence of 5 with preferential insertion of allene residue into the C-O bond of 5.

It has been known that rhodium complexes are highly effective catalyst for oligomerization of allene.[12)] Thus, treatment of 1 with $RhCl(PPh_3)_3$ in the presence of allene caused oligomerization of the latter only, leaving the ester 1 almost intact (Table 1). This may exclude the intermediacy of free allene in the course of the reaction depicted in Scheme 1. Although further experiments need to be performed in order to gain additional insight into the process, a tentative reaction path is shown in Scheme 2. Oxidative addition of the allylic ester 1 to Rh(I)-species will form the π-allylic complex 13.[3a)] Abstraction of the C_2-proton by chloroacetate anion may give chloroacetic acid and allene residue complexed with

Scheme 2.



rhodium (14). Interaction of 14 with allyl ester 1 or π-allyl species 13 may give rise to another π-allylrhodium complex 15, and reductive elimination of 2 will regenerate active Rh(I)-species.

Release of a β-methylene proton of π-allylpalladium species has been well demonstrated to give 1,3-diene in the palladium chemistry.[13] To our knowledge, however, elimination of allene unit from π-allyl-metal complexes, even though in a formal sense, seems unprecedented.

References

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3. a) G. P. Chiusoli, Pure Appl. Chem., 52, 635 (1980); b) M. Wayaku, K. Kaneda, T. Imanaka, and S. Teranishi, Bull. Chem. Soc. Jpn., 48, 1957 (1975).
4. For another metal-catalyzed C-O bond cleavage, see, for example, T. Yamamoto, J. Ishizu, and A. Yamamoto, J. Am. Chem. Soc., 103, 6863 (1981), and literatures cited therein.
5. 2: Found(Calcd): C, 55.09(55.01); H, 6.37(6.35); Cl, 19.98(20.31). ^{1}H NMR (CCl_4, hexamethyldisiloxane) δ2.75(2H, d-like), 3.9(2H, s), 4.5(2H, s(br)), 4.6-5.3(4H, m), 5.3-6.0(1H, m). IR(liq. film) 1750, 1660, 1640, 1300, 1160, 995, 915 cm^{-1}.
   3: ^{1}H NMR(acetone-d_6) δ4.1(2H, s), 10.6(1H, s).
   4: Found(Calcd): C, 54.72(55.01); H, 6.28(6.35); Cl, 20.04(20.31). ^{1}H NMR (CCl_4) δ3.85 and 3.90(s, $ClCH_2CO$- for *E*- and *Z*-4). IR(liq. film) 1750, 1670, 1640, 1300, 1160, 980, 920 cm^{-1}.
6. After the reaction, standing of the reaction mixture for 1 to 2 days at room temperature caused precipitation of orange-yellow crystals, which showed similar IR spectrum with that of $RhCl(CO)(PPh_3)_2$; IR(KBr) 1970 cm^{-1} (νCO).
7. Cf. H. Suzuki, Y. Koyama, Y. Moro-oka, and T. Ikawa, Tetrahedron Lett., 1979, 1415.
8. The chloroacetates were prepared by reaction of chloroacetyl chloride and respective allylic alcohols in the presence of slightly excess amount of pyridine. 1: bp 72-75°C/25.5 mmHg. 6: bp 83.0°C/29 mmHg. 7: bp 77.2°C/12.5 mmHg. 8: bp 74.5°C/15.5 mmHg.
9. 11: ^{1}H NMR(CCl_4) δ2.7(2H, d-like), 4.5(2H, s(br)), 4.7-5.2(4H, m), 5.3-5.7 (1H, m), 5.8(1H, s). IR(liq. film) 1740, 1650, 1640, 1300, 1160, 990, 910 cm^{-1}.
10. E. J. Corey and J. W. Suggs, J. Org. Chem., 38, 3224 (1973).
11. 10: ^{1}H NMR(CCl_4) δ1.95(3H, s), 2.7(2H, d-like), 4.3(2H, s(br)), 4.6-5.2(4H, m), 5.3-5.8(1H, m). IR(liq. film) 1750, 1660, 1640, 1230, 995, 910 cm^{-1}.
12. a) S. Otsuka, K. Tani, and A. Nakamura, J. Chem. Soc. (A), 1969, 1404; b) S. Otsuka, A. Nakamura, and K. Tani, Kogyo Kagaku Zasshi, 70, 2007 (1967); c) F. J. Jones and R. V. Lindsey, Jr., J. Org. Chem., 33, 3838 (1968).
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(Received June 11, 1982)