CHEMISTRY LETTERS, pp. 1071-1074, 1986.

ELECTROPHILIC REACTION OF ALLYL ACETATES WITH ELECTROGENERATED CARBANIONS IN THE PRESENCE OF Pd(0)-CATALYST

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Counter cation effect on the Pd(0)-catalyzed electrophilic reaction of allyl acetates with carbanions was studied by using the electrogenerated carbanions having various kinds of counter cations.

Generally, reactivity of anionic nucleophiles is affected by their counter cations. However, in most cases it is not easy to prepare the nucleophiles having the desired counter cations. Anionic species generated at cathodes have the counter cations derived from the supporting salts used. Therefore, there has been currently considerable interest in reactions using the electrogenerated anions.[1,2] For example, in previous works we developed some reactions using the electrogenerated anions as base catalysts,[3,4] reducing reagents,[5] and nucleophiles.[4,6]

Although the reaction of allylic compounds with carbanions in the presence of Pd(0)-catalysts has been extensively studied,[7] there has been no study on the counter cation effect on this reaction.[8]

From these view points, we studied on the influence of counter cations on the Pd(0)-catalyzed electrophilic reaction of allyl acetates with carbanions by using the electrogenerated carbanions having various kinds of counter cations as shown in Scheme 1.

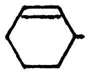
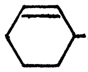
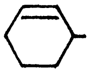
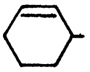
$$\mathrm{RH} + \mathrm{X^-M^+} + \mathrm{e} \longrightarrow \mathrm{R^-M^+} \qquad \text{RH: Active hydrogen compound} \quad \mathrm{X^-M^+}\text{: Supporting salt}$$

$$\mathrm{R'R''C{=}CHCHR'''\,OAc} + \mathrm{R^-M^+} \xrightarrow[\text{Pd(0)-complex catalyst}^{9)}]{} \mathrm{R'R''C{=}CHCHR'''\,R} + \mathrm{AcO^-M^+}$$

Scheme 1.

The reaction was first examined by using simple unsubstituted and 3-monosubstituted allyl acetates. A typical reaction procedure is as follows: The cathodic solution containing active hydrogen compound(3.0-12.0 mmol), Ph_3P(0.7 mmol), Pd(II)$(PhCN)_2Cl_2$(0.10 mmol), supporting salt(0.5 mol dm^{-3}) in dry DMF(30 cm^3) was electrolyzed using a Pt cathode at 0.26 A dm^{-2} of current density under nitrogen atmosphere in a divided cell, and then allyl acetate(2.0-3.8 mmol) was added. The reaction mixture was allowed to stand for 12 h at room temperature. In a chemical method, NaH was used instead of passing electricity. Reaction conditions used and results obtained are summarized in Table 1.

Table 1. Pd(0)-Catalyzed Reaction of Unsubstituted and 3-Monosubstituted Allyl Acetates with Carbanions Generated Cathodically and Chemically from the Corresponding Active Hydrogen Compounds in DMF

Run	Allyl acetate (mmol)	Active hydrogen compound (mmol)	Supporting salt	Charge passed / mF a)	NaH / mmol	Product yield b) / %
1	$CH_2=CHCH_2OAc$(3.0)	$CH_2(COOCH_3)_2$(3.0)	Et_4NClO_4	3.2	-	54
2	$CH_2=CHCH_2OAc$(3.0)	$CH_2(COOCH_3)_2$(3.0)	$NaClO_4$	3.2	-	63
3	$CH_2=CHCH_2OAc$(3.0)	Fluorene(3.0)	Et_4NClO_4	3.2	-	81
4	$CH_2=CHCH_2OAc$(3.0)	Fluorene(3.0)	$NaClO_4$ c)	3.2	-	0 d)
5 e)	$CH_2=CHCH_2OAc$(3.0)	Fluorene(3.0)	-	-	3.0	50
6 f)	OAc(3.8)	CH_3NO_2(12.0)	Et_4NClO_4	13.2	-	35
7 f)	OAc(3.5)	CH_3NO_2(12.0)	Bu_4NClO_4 c)	13.2	-	45
8 f,g)	OAc(3.5)	CH_3NO_2(12.0)	$NaClO_4$ c)	13.2	-	0 d)
9 e)	OAc(3.5)	CH_3NO_2(12.0)	-	-	12.0	0 d)

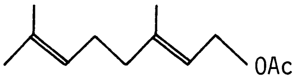
a) 1 F=96485 C. b) Based on the allyl acetate. c) 0.4 mol dm^{-3}. d) Large amounts of the starting materials were recovered. e) Chemical method using Ph_3P (0.3 mmol) and $Pd(0)(Ph_3P)_4$(0.10 mmol). f) Electrolyzed at 0.39 A dm^{-2}. g) Reacted for 16 h.

In the reaction of unsubstituted allyl acetate with dimethyl malonate, any significant difference was not observed between supporting salts of Et_4NClO_4(Run 1) and $NaClO_4$(Run 2), whereas a remarkable difference was observed in the case of fluorene(pKa ca. 23), less acidic than the malonate(pKa ca. 13). The reaction using Et_4NClO_4(Run 3) gave a high product yield(81%), while no product was obtained using $NaClO_4$(Run 7). This fact may be rationalized as due to the more negative reduction potential of fluorene than that of sodium cation:10) Not fluorene but sodium cation might be cathodically reduced in Run 4. This was also confirmed by another fact that the reaction could take place in the chemical method(Run 5). A lower yield in the chemical method using NaH suggests that the carbanion, $^-CH(COOCH_3)_2$ having Na^+ as the counter cation is a less active nucleophile than that having Et_4N^+.

The reaction of nitromethane(pKa ca. 10), more acidic than the malonate, was examined by using 3-acetoxycyclohexene as an allyl acetate. Only the cathodic method using quaternary ammonium salts(Runs 6 and 7) could result in the formation of the desired product, while neither the cathodic one using $NaClO_4$(Run 8) nor the chemical one using NaH(Run 9) gave any product. This fact suggests that the carbanion $^{-}CH_2NO_2$, which is derived from strongly acidic nitromethane and has a nature of low nucleophilicity, can be activated only by having quaternary ammonium cations of no Lewis-acidity as the counter cations.

As a conclusion, it is stated that the cathodic method using quaternary ammonium salts can be favorably used for the reaction of both weakly and strongly acidic active hydrogen compounds.

Next, more complicated 3,3-disubstituted allyl acetates were used to investigate regio- and stereoselectivities of the reaction. Trost and Verhoeven[11)] reported that geranyl acetate(**1**) reacted with $Na^{+-}CH(COOCH_3)_2$ in THF under reflux to give the inner olefin(**3**) and outer olefin(**4**) (**3**:**4**=87:13), while neryl acetate(**2**) gave the inner olefin(**5**) and **4**(**5**:**4**=35:65). They did not detect any isomerized product[12)] in the reaction.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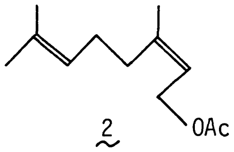
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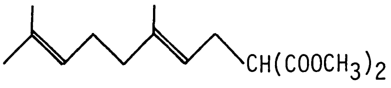
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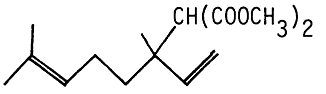
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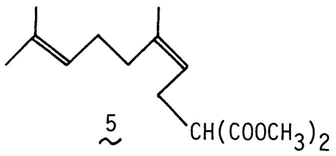
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On the contrary, as shown in Table 2, **1** and **2** gave the isomerized products **5** and **3**, respectively, in considerable yields when quaternary ammonium salts were used as supporting electrolytes. On the other hand, the isomerization scarcely took place in the reaction using $NaClO_4$(Runs 10, 18, and 21). The isomerization in the case of **1** took place in DMF(Runs 11 and 12) rather than in THF(Rund 13 and 16), which is contrary to the case of **2**(Runs 19 and 20). It is difficult at present to explain clearly the observed counter cation and solvent effects on the regio- and stereoselectivities, though the effects may be partly explained on the basis of a hard-soft theory.

Tertiary sulfonium cation resembles quaternary ammonium one in a saturated closed shell structure and often shows similar chemical properties. The isomerization similarly took place in the reaction using Et_3SClO_4(Runs 17 and 23), although such isomerization scarcely occurred in DMF(Run 14). It is noticeable that the counter cation effect of sulfonium was superior to that of quaternary ammonium as observed in Run 15.

Furthermore, an interesting effect of ligand of Pd(0)-complex was also observed. Thus, the total yields of the products remarkably increased by changing Ph_3P to a bident ligand[Ethylene bis(diphenylphosphine),DIPHOS] under mild conditions(Run 17). In the reaction of **2** using DIPHOS(Runs 22 and 23), not only the yield but also the product distribution was greatly affected.

Thus, this work demonstrated that the cathodic method has an advantage as follows: The reactivities such as nucleophilicity, and regio- and stereoselectivities of carbanions can be controlled by the selection of counter cations of supporting electrolytes.

Table 2. Pd(0)-Catalyzed Reaction of 3,3-Disubstituted Allyl Acetates[a] with Carbanions Generated Cathodically from Dimethyl Malonate[b]

Run	Allyl acetate	Supporting salt	Solvent	Reaction temperature	Product distribution/%			Total yield[c]
				°C	3	4	5	%
10	1	$NaClO_4$	DMF	55-60	77	22	1	48
11	1	Et_4NClO_4	DMF	55-60	56	33	11	76
12	1	Bu_4NClO_4	DMF	55-60	63	28	9	57
13	1	Bu_4NClO_4	THF	reflux	75	20	5	77
14	1	Et_3SClO_4	DMF	55-60	87	12	1	27
15	1	Et_4NClO_4-Et_3SClO_4[d]	DMF	55-60	88	10	2	24
16[e]	1	Bu_4NClO_4	THF	r.t.	83	13	4	91
17[e]	1	Bu_3SClO_4	THF	r.t.	86	6	8	78
18[f]	2	$NaClO_4$	DMF	55-60	0	80	20	50
19[f]	2	Et_4NClO_4	DMF	55-60	5	64	31	75
20[f]	2	Bu_4NClO_4	THF	reflux	19	48	33	70
21[f]	2	$NaClO_4$	THF	reflux	0	65	35	80
22[e,f]	2	Bu_4NClO_4	THF	r.t.	15	19	66	98
23[e,f]	2	Bu_3SClO_4	THF	r.t.	20	13	67	75

a) 2.0 mmol. b) The malonate(8.0 mmol) was electrolyzed by passing 12.0 mF under the conditions similar to those in Table 1. c) Based on the starting allyl acetate. d) A small amount(9 mmol) of Et_3SClO_4 was added after the electrolysis. e) Ethylene bis(diphenylphosphine)(DIPHOS) was used instead of Ph_3P. f) Electrolyzed passing 5.6 mF at 0.7 A dm^{-2} and -10 °C.

References 1) M. M. Baizer, Tetrahedron, 40, 935 (1984). 2) T. Shono, "Electroorganic Chemistry as a New Tool in Organic Synthesis," Springer-Verlag, Berlin (1984). 3) T. Komori, T. Nonaka, and T. Fuchigami, Chem. Lett., 1986, 11. 4) T. Fuchigami, T. Awata, T. Nonaka, and M. M. Baizer, Bull. Chem. Soc. Jpn., submitted for publication. 5) T. Takiguchi and T. Nonaka, Nippon Kagaku Kaishi, 1985, 1147. 6) T. Awata, M. M. Baizer, T. Nonaka, and T. Fuchigami, Chem. Lett., 1985, 371. 7) J. Tsuji, T. Takahashi, and I. Shimizu,"Yukigosei No Saizensen," ed by T. Mukaiyama and G. Tsuchihashi, Tokyo Kagaku Dojin, Tokyo(1985), p.171. 8) In most cases, alkali metal cations have been used as the counter cations. 9) Since the preparation of Pd(0)-catalyst is troublesome and it can not be stored for a long time owing to its unstability, the catalyst was electrochemically generated in situ from Pd(II)-complex. 10) It is well-known that reduction potentials of quaternary ammonium cations are much more negative than those of alkali metal ones. 11) B. M. Trost and T. Verhoeven, J. Am. Chem. Soc., 102, 4730 (1980). 12) They rationalized no occurrence of isomerization in the course of the reaction as due to a slower rate of the syn-anti isomerization of π-allyl-palladium complex intermediates than that of nucleophilic attack of $^{-}CH(COOCH_3)_2$ to the intermediates.

(Received April 4, 1986)