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PALLADIUM-CATALYZED REACTION OF NUCLEOPHILES WITH DIACETATES OF ALLYLIC 1,1-DIOLS

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Summary

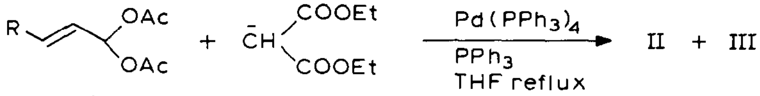
The reactions of allylic 1,1-diol diacetates (I) with carbanions under the catalysis of $Pd(PPh_3)_4$ were studied. Sodium diethyl malonate reacted with I to form an abnormal product resulting from the attack of the diethyl malonate carbanion on the carbonyl carbon of the acetoxy group, while sodium diethyl acetylmalonate gave the normal reaction products with high regioselectivity. The mechanisms of these reactions are discussed.

Introduction

The reaction of allylic acetates with nucleophiles in the presence of $Pd(PPh_3)_4$ as catalyst has been extensively studied by Trost and widely used in organic synthesis due to its high chemoselectivity, regioselectivity and stereoselectivity [1]. It is interesting to study the reaction of nucleophiles with compounds having two leaving groups on the same carbon atom at the allylic position.

Results and discussion

The 3-substituted 1,1-diacetoxy-2-propenes (I) could be easily prepared from α,β-unsaturated aldehydes and acetic anhydride in high yield [2]. The reaction of compounds I with sodium diethyl malonate under the catalysis of $Pd(PPh_3)_4$ was examined.



(I)

(a, R = H; b, R = CH_3, c, R = Ph)

Compound Ib was refluxed with sodium diethyl malonate in THF. The starting material Ib disappeared after 7 h and ^1H NMR spectra indicated the presence of a

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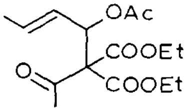
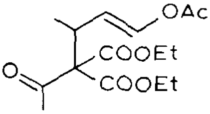
large amount of diethyl malonate (δ 3.2 ppm) and of an aldehyde group (δ 9.6 ppm). After separation by column chromatography, an oily product was obtained in 43% yield which was proved to be a mixture of IIb and IIIb (IIb/IIIb = 7/1) according to IR, NMR and MS analyses.



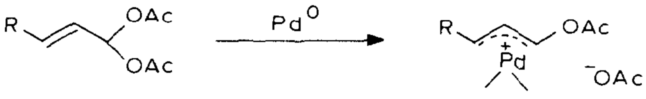
(IIb)



(IIIb)

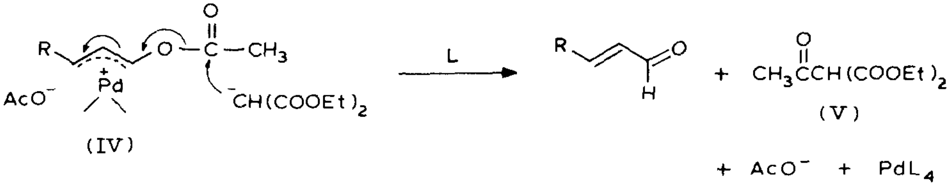
When Ic was used as the starting material, cinnamic aldehyde was isolated in 30% yield.

From the formation of the reaction product, diethyl malonate and the aldehyde, it is suggested that the π-allyl Pd complex is formed at first by the oxidative addition of the C–O bond of one of the acetoxy groups to the zero valent palladium and then



(I) (IV)

the malonate carbanion attacks the carbon atom of the carbonyl group of the remaining acetoxy group to form diethyl acetylmalonate and α,β-unsaturated aldehyde as shown in the following scheme:



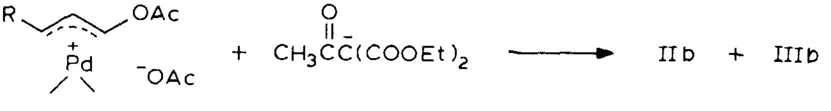
(IV) (V)

Proton transfer then occurs from the unreacted malonate carbanion to diethyl acetylmalonate to give diethyl malonate:

$$\underset{(V)}{CH_3\overset{O}{\overset{\|}{C}}CH(COOEt)_2} + {}^-CH(COOEt)_2 \rightleftharpoons \underset{(VI)}{CH_3\overset{O}{\overset{\|}{C}}\bar{C}(COOEt)_2} + CH_2(COOEt)_2$$

(V) (VI)

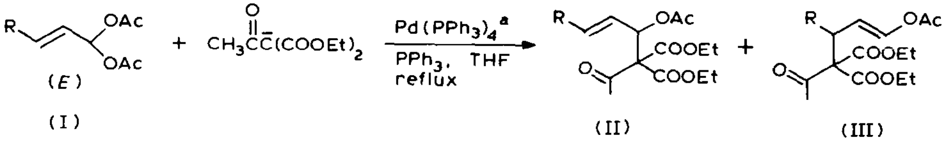
Finally, the carbanion VI attacks the remaining π-allyl Pd complex IV to give the isolated products, IIb and IIIb.



(IVb) (VI)

TABLE 1

REACTION OF SODIUM DIETHYL ACETYLMALONATE WITH I



Compound	R	Time (h)	Yield [b] (%)	Product [c] II	Product [c] III
a	H	4	71	75	25 (*E*)
b	CH_3	7	80	93 (*E*)	7 (*E*)
c	Ph	18	75	100 (*E*)	0

[a] 5 mol%. [b] Isolated yield. [c] Determined by NMR.

Sodium diethyl malonate could react neither with Ib in the absence of $Pd(PPh_3)_4$ nor with 1,1-diacetoxybutane in the presence of $Pd(PPh_3)_4$. These facts strongly indicate that the allylic linkage and the Pd catalyst are important in the attack of the carbanion on the carbonyl carbon atom of the acetoxy group.

In order to prove this suggested mechanism, sodium diethyl acetylmalonate was used as the nucleophile to react with Ib. Indeed, IIb and IIIb were obtained as the reaction products with the same NMR and IR spectra as those obtained from malonic ester as the carbanion. Interestingly in all cases, the attack of acetylmalonate carbanion on π-allyl carbon did occur and II and III were obtained as shown in Table 1. In no case was diethyl diacetylmalonate isolated, further demonstrating that the diethyl acetylmalonate anion did not attack the carbonyl carbon atom of the acetoxy group. In other words, the carbanion of diethyl acetylmalonate attacked the carbon atom of the π-allyl group. The steric effect of the R group may have some influence on the regioselectivity. When R is the bulky phenyl group (Ic), only IIc was obtained. It is interesting to note that even when R is H (Ia), a regioselectivity of 75% to give IIa was still obtained.

All the disubstituted olefins obtained were in *E* form as indicated by the NMR (J 12–15.4 Hz) and IR (ν 970 cm^{-1}) spectra. This may result from the *syn*-configuration of the π-allylpalladium intermediate and is consistent with other work [1].

The study of the reason why malonate anion attacks the carbonyl carbon atom of the acetoxy group, while the acetylmalonate anion prefers to attack the carbon atom of the π-allyl group, and the study of the difference in the position of attack by different nucleophiles are being done.

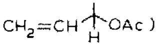
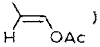
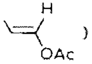
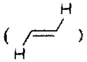
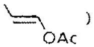
Experimental

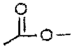
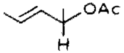
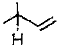
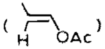
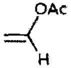
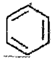
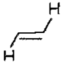
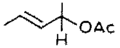
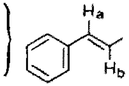
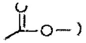
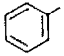
All reactions were carried out under prepurified nitrogen or argon using Schlenk's technique. Compounds I were prepared according to the literature [2]. All solvents and starting materials were distilled under nitrogen before use. ^1H NMR spectra were recorded on an EM-360 or Varian XL-200 spectrometer. Infrared spectra were taken as liquid films using a SPECORP 75 IR spectrometer. Mass spectra were obtained on a Finnigen 4021 GC/MS/DC instrument.

(Continued on p. 190)

TABLE 2

SPECTRAL AND ANALYTICAL DATA OF II AND III

Compound	^{1}H NMR (CDCl$_3$/TMS) (ppm)	IR (cm^{-1})	Molecular formula	MS (m/e)	B.p. (°C/mmHg)	Elementary analysis (Found (calcd.)(%))	
						C	H
IIa	1.3 (t, 6H, J 7 Hz, CH_3)	910, 995s ($CH=CH_2$)	$C_{14}H_{20}O_7$	301(M^+ +1)	108–110/0.1	55.73	6.73
	2.05 (s, 3H, $CH_3C(O)O$)	960s	(300.30)			(55.99)	(6 71)
	2.32 (s, 3H, $CH_3C(O)$)	1660m ()					
	4.3 (q, 4H, J 7 Hz, OCH_2)	1705vs (C=O)					
	5.2–6.3 (m, 4H, )	1720–1735vs (two peaks, )					
IIIa	1.3 (t, 6H, J 7 Hz, CH_3)						
	2.1 (s, 3H, $CH_3C(O)O$)						
	2.32 (s, 3H, $CH_3C(O)$)						
	2.7 (d, 2H, J 8 Hz, $CH_2CH=C<$)						
	4.3 (q, 4H, J 7 Hz, OCH_2)						
	5.1 (m, 1H )						
	7.12 (d, 1H, J 12.5 Hz 						
IIb	1.28 (t, 6H, CH_3)	970s ()	$C_{15}H_{22}O_7$	315(M^+ +1)	116/0.1	56.88	6.94
	1.69 (d, 3H, J 6 Hz, $CH_3C=C$)	1640w (C=C)	(314.33)			(57.31)	(7.66)
	2.05 (s, 3H, $CH_3C(O)O$)	1660m ()					
	2.34 (s, 3H, $CH_3C(O)$)	1720vs (C=O)					

	4.3 (q, 4H, J 7 Hz, OCH_2)	1730–1745vs					
	5.5–5.9 (m, 2H, CH=CH)	(two peaks, )					
	6.05 (d, 1H, J 6.5 Hz, )						
IIIb	1.19 (d, 3H, J 8 Hz, CH_3) 1.28 (t, 6H, J 7 Hz, CH_3CH_2) 2.0 (s, 3H, $CH_3C(O)O$) 2.3 (s, 3H, $CH_3C(O)$)						
	3.25 (m, 1H, )						
	4.3 (q, 4H, J 7 Hz, $-OCH_2-$)						
	5.05 (m, 1H, ()						
	7.15 (d, 1H, J 12.5 Hz, )						
IIc	1.28 (t, 6H, J 7 Hz, CH_3C)	690, 760s ()	$C_{20}H_{24}O_7$	376(M^+)	160/0.1	64.13 (63.82)	6.51 (6.43)
	2.08 (s, 3H, $CH_3C(O)O$)	970s ()	(376.39)				
	2.35 (s, 3H, $CH_3C(O)$) 4.3 (q, 4H, J 7 Hz, OCH_2)	1640m (C=C) 1720vs ($>$C=O)					
	6.23 (d, 1H, J 6.6 Hz, )	1730–1745vs					
	6.4 (d,d, $1H_b$, J 15.4, 6.6 Hz) 6.66 (d, $1H_a$, J 15.4 Hz 	(two peaks, )					
	7.3 (m, 5H, )						

An example of reaction using diethyl malonate anion as the nucleophile

After stirring a mixture of *trans*-1,1-diacetoxy-2-butene (Ib, 930 mg, 5.4 mmol), $Pd(PPh_3)_4$ (280 mg, 0.24 mmol), Ph_3P (260 mg, 1 mmol) and THF (10 ml) for 15 min, sodium diethyl malonate (6 mmol in 15 ml THF, prepared from diethyl malonate and sodium hydride) was added with a syringe. A large amount of solid was precipitated after the mixture was refluxed for 7 h and TLC (silica gel/ethyl acetate/petroleum ether 1/5) showed the disappearance of Ib. On removing THF, ether (40 ml) was added and the ether layer was washed with ice water three times (15 ml each). The water layer was again extracted with ether (30 ml) twice and the combined ether extract, after being dried with anhydrous sodium sulfate, was evaporated. The residue was purified by column chromatography using silica gel and petroleum ether/ethyl acetate (5/1) as the solvent. The oil (730 mg) obtained was proved to be a mixture of IIb and IIIb with a ratio of 7/1 by NMR, IR and MS spectra, yield 43%. From another fraction, diethyl malonate (290 mg) was also isolated.

An example of reaction using diethyl acetylmalonate anion as the nucleophile

After stirring a mixture of *trans*-1,1-diacetoxy-2-butene (Ib, 540 mg, 3.0 mmol), $Pd(PPh_3)_4$ (160 mg, 0.14 mmol), Ph_3P (160 mg, 0.6 mmol) and THF (10 ml) for 15 min, sodium diethyl acetylmalonate (3 mmol in THF 10 ml, prepared from diethyl acetylmalonate and sodium hydride) was added with a syringe. The reaction mixture was monitored with TLC (silica gel/ethyl acetate/petroleum ether 1/5) and Ib disappeared after refluxing 7 h. The reaction mixture was treated as above and chromatographed on silica gel using petroleum ether (30–60°C)/ethyl acetate (5/1) as the eluent. The oil (750 mg, b.p. 116°C/0.1 mmHg) obtained was proved to be a mixture of IIb and IIIb with a ratio of 93/7 by NMR, IR, MS and elementary analyses, yield 80%.

The data of ^1H NMR, IR, MS and elementary analyses of compounds II and III are given in Table 2.

Acknowledgements

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