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C-H Bond Cleavage in Alkenyl Carboxylates Promoted by Methylcopper Complexes and Formation of Six-Membered Acetoxyvinylcopper Chelates

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Summary

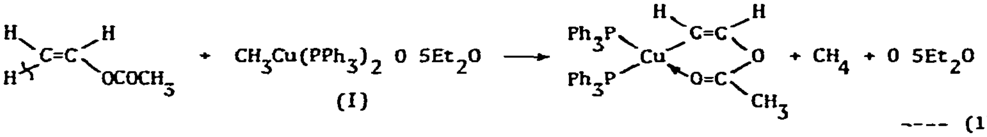
Methylbis(triphenylphosphine)copper(I) etherate (I) reacts with vinyl acetate, evolving methane to form a six-membered cyclic product, 2-acetoxyvinylbis(triphenylphosphine)copper(I) (II) A similar reaction involving cleavage of the C-H bond adjacent to the double bond proceeds also with isopropenyl acetate, giving 2-acetoxy-1-propenylbis(triphenylphosphine)copper(I) (III)

Introduction

Selective cleavage of a C-H bond in an organic compound promoted by a transition metal compound under mild conditions is currently attracting growing attention Substitution of olefins promoted by palladium compounds [1] and H-D exchange in aliphatic and aromatic hydrocarbons catalyzed by platinum, palladium, titanium, and niobium compounds [2], as well as some types of ethylene dimerization [3], are considered to proceed through oxidative addition reactions of the hydrocarbons to transition metal complexes involving cleavage of a C-H bond. However, unequivocal, established examples of such oxidative addition are limited to a few cases, such as the orthometallation [4] in which C-H bond cleavage of a coordinated tertiary phosphine ligand or of aromatic ketones [5] is involved, and the recently reported reactions of osmium complexes with ethylene [6], of iridium complexes with aromatic azo or imine compounds [7] and of alkyl methacrylates with a ruthenium complex [8]. In the last case, the cleavage of a C-H bond adjacent to a C=C bond in alkyl methacrylates gave oxidative addition products with a five-membered ring. We now report another example of such selective C-H bond cleavage observed in the reaction of $CH_3Cu(PPh_3)_2 \cdot 0.5Et_2O$ (I) with vinyl and isopropenyl acetate which gives six-membered organocopper chelates. The result is in contrast with the reaction of vinyl and isopropenyl acetate with $RuH_2(PPh_3)_4$ which caused the cleavage of the C-O bond in the esters releasing ethylene and propylene [9]

Results and Discussion

The methylcopper complex, $CH_3Cu(PPh_3)_2$ $0.5Et_2O$ (I) [10-12], reacts with vinyl acetate to give a six-membered chelate complex, 2-acetoxyvinylbis(triphenylphosphine)copper(I) (II).


(I) (II)

---- (1)

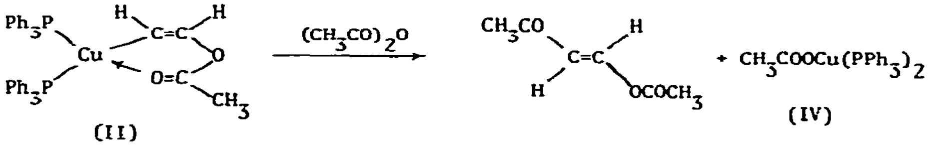
The reaction proceeds smoothly at 0°C evolving 1 mol of methane per mol of I to give a white precipitate of II in a high yield The other methylcopper complexes having tertiary phosphine ligands other than triphenylphosphine behave similarly The structure of II has been deduced on the basis of its elemental analysis, molecular weight determination (found 640 ± 10 cryoscopic in benzene, calcd 673), its chemical reactions, IR and NMR spectroscopy. The ^1H-NMR spectrum of II showed two doublet signals at δ 5.23 and 8.62 with a coupling constant of 7Hz, in addition to the acetate methyl signal at δ 1 93 and signals due to the triphenylphosphine ligands The doublets at δ 5 23 and 8.62 may be ascribed to protons attached to the double bond and the coupling constant of 7Hz suggests that the protons are at mutually cis positions It is noted that the proton attached to the carbon adjacent to oxygen is very much deshielded. The assignment was made also by comparing the ^{1}H-NMR spectrum of II with that of the reaction product of I with isopropenyl acetate

The ^{31}P-{^{1}H}-NMR spectrum of II in toluene containing C_6D_6 at room temperature shows a broad singlet at 0 2 ppm downfield from the external PPh_3 reference in toluene The signal sharpens somewhat and shifts to 1.1 ppm downfield from PPh_3 on cooling the solution to -80°C, but no peak due to free triphenylphosphine was observed The solution containing two moles of PPh_3 per II at -80°C showed two overlapping ^{31}P signals due to free PPh_3 and II at 1 4 ppm downfield from PPh_3 in an approximate area ratio of 1 1 which collapsed to a broad singlet on raising the temperature These results, together with the slightly low observed value of the molecular weight for II, suggest that complex II dissociates a minor amount of PPh_3 at room temperature and the liberated PPh_3 exchanges with the coordinated PPh_3 in II.

The IR spectrum of II shows ν(C=O) at 1605 cm^{-1} which is shifted about 170 cm^{-1} to lower frequency from ν(C=O) in free vinyl acetate The large shift of ν(C=O) strongly suggests the formation of a six-membered ring containing the C=O group bonded to copper. Similar shifts of ν(C=O) to low frequency on chelate formation of carboryl compounds with transition metal complexes have been observed [5,8] The methane evolved in the reaction of I with vinyl acetate is considered to be formed by abstraction of hydrogen from vinyl acetate, presumably by a process involving the oxidative addition of vinyl acetate to copper followed by reductive elimination of the methyl and hydrido ligands from an unstable copper(III) intermediate. The possibility that hydrogen abstraction occurred by involvement of orthometallation of the triphenylphosphine ligands was excluded since the reaction of vinyl acetate with $CH_3Cu(PPh_3\text{-}d_6)_2\cdot 0.5Et_2O$ [11], in which 98.0 % of the ortho-hydrogens in the triphenylphosphine ligands were deuterated, liberated CH_4 almost exclusively, with only a trace of CH_3D.

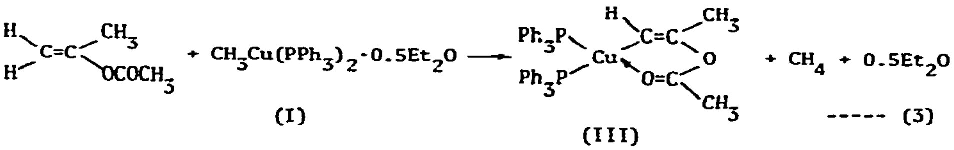
Complex II shows a remarkable thermal stability for an organocopper complex [11,12] and is not decomposed by heating for 10 hours at 60°C in benzene In contrast to the photosensitivity of the starting methylcopper complex I, irradiation of II with a high pressure mercury lamp for a day at room temperature caused no decomposition of II.

In order to examine the reactivity of complex II, the reactions of acetic anhydride and acetyl bromide with II at room temperature were carried out and a volatile product produced was identified as trans-4-acetoxy-3-buten-2-one [13] with yields of 58 and 61 %, respectively. The results indicate that inversion of configuration occurred during the reactions since complex II most probably possesses a cis-form with respect to the C=C bond In the reaction of II with acetic anhydride, acetatobis(triphenylphosphine)copper(I) (IV) [14] was recovered as a white solid The acetatocopper complex was characterized by comparison of its IR and NMR spectra with those of the sample prepared by the reaction of I with carbon dioxide or acetic acid [15]



(2)

The similar reaction of I with isopropenyl acetate afforded a related six-membered chelate (III)



(3)

The reaction proceeded smoothly at low temperature with evolution of 1 mol eq of methane and a white precipitate was formed Upon repeated recrystallization, complex III was separated from the white precipitate which contained acetatobis(triphenylphosphine)copper (vide infra) The proton NMR spectrum of III shows the methyl signal (6H, s) at δ 2 00 ppm which arises from accidental coincidence of the methyl signal of the acetyl group in III with that of the methyl group in the propenyl moiety. The proton attached to the C=C bond resonates at δ 5.42 (1H, s) As in the proton NMR spectrum of II, the ortho protons of the triphenylphosphine ligands in III appeared at lower field as a multiplet centering around δ 7 6 (12H) than the meta and para protons at δ 7 0 (18H, multiplet) The large shift of ν(C=O) in complex III to lower frequency (1595 cm^{-1}) than in the free isopropenyl acetate was also observed in this case as in II Complex III was found to be very stable, heating of III at 80°C in toluene, treatment of III with isopropenyl acetate for a day at room temperature, or UV irradiation of III for a day at room temperature caused no decomposition of III

The reaction (3) giving complex III was accompanied by formation of the acetatocopper complex IV Since IV was always formed even when carefully purified acid-free isopropenyl acetate was used, the reaction of I with isopropenyl acetate is considered to be accompanied by C-O cleavage in addition to the C-H bond cleavage The C-O bond cleavage of carboxylic esters promoted by zero-valent nickel complexes has been recently reported [16] and the acetatocopper complex in the present case may have been similarly produced, although attempts to identify the residue from the C-O bond cleavage have failed The reactions of I with other acetate esters such as allyl, benzyl and phenyl acetate also gave IV. The details of these reactions will be reported separately.

Experimental

General

All preparations and recrystallizations of copper complexes were carried out under deoxygenated nitrogen, argon, or in a vacuum. Solvents were dried by usual procedures, distilled, and stored under argon or nitrogen. IR spectra were recorded on a Hitachi Model 295 using KBr discs under nitrogen Proton and $^{31}P\{^{1}H\}$-NMR spectra were recorded with a Japan Electron Optics Lab. JNM-PS-100 spectrometer (TMS as an internal standard for ^{1}H-NMR and triphenylphosphine as an external standard for $^{31}P\{^{1}H\}$-NMR) Evolved gas was analyzed with a Hitachi RMU 5B mass-spectrometer and a Shimadzu GC-5B gas chromatograph, and its volume was measured with a Toepler pump. The microanalysis of carbon, hydrogen and nitrogen was performed by Mr. T. Saito in our laboratory with a Yanagimoto CHN Autocorder Type MT-2. Vinyl acetate (free acid 0 01 %) and isopropenyl acetate (free acid < 0 03 % after purification) were reagent grade commercial products and were distilled over CaH_2 or $CaSO_4$ before use

1. Reaction of $CH_3Cu(PPh_3)_2$ 0 5Et_2O (I) with vinyl acetate

Complex I was prepared as reported previously [10] Vinyl acetate (5 0 ml) was introduced into a Schlenk type flask containing I (1.00 g, 1 56 mmol) by a trap-to-trap distillation in a vacuum The yellow suspension gradually turned white and a white precipitate (867 mg, yield 87 %) of 2-acetoxyvinylbis(triphenylphosphine)copper(I) (II) was formed at 0°C in a day with simultaneous evolution of methane (35 2 ml, S T P , 0 98 mol per mol of I). The precipitate was recrystallized from toluene or a mixture of tetrahydrofuran and diethyl ether to give fine white crystals which were washed with hexane and dried in a vacuum. Complex II melted with decomposition at 192°C. (Found· C, 71.6; H, 5.7; Cu, 9.5. $C_{40}H_{35}O_2Cu$ calcd.· C, 71.4; H, 5.2; Cu, 9.4 %) IR: $\nu(C=O)$ 1605 cm^{-1}

^{1}H-NMR (C_6D_6) δ 1.92 (s, 3H, CH_3); δ 5.23 (d, 1H, J = 7 Hz, =CH); δ 7 0 (multiplet, 18H, m, p-phenyl); δ 7 6 (m, 12H, o-phenyl); δ 8.62 (d, 1H, J = 7 Hz, =CH). $^{31}P\{^1H\}$NMR (toluene) δ 0 2 (broad). Molecular weight of II (cryoscopic in benzene) 640 (calcd 673) The mass spectrum of the thermolysis products of II shows the parent peak of vinyl acetate at m/e of 86.

The reaction of vinyl acetate (5 0 ml) with methylcopper complex containing orthodeuterated triphenylphosphine, $CH_3Cu(PPh_3\text{-}d_6)_2 \cdot 0.5Et_2O$ (652 mg, 1 mmol, isotopic purity 98 %. see ref. (11)) was conducted similarly After the reaction at -30°C to room temperature for a day, production of CH_4 (14 1 ml, S T P., 0 63 mmol per mmol of methylcopper) and of a small amount of CH_3D (0 04 mmol) was confirmed by mass spectrometric examination

Reaction of II with $(CH_3CO)_2O$ and CH_3COBr

Acetic anhydride (5 0 ml) was added to complex II (2 69 g, 4 mmol) at room temperature and the reaction mixture was stirred under N_2 atmosphere. After 30 min, complex II was dissolved and white crystals of acetatobis(triphenylphosphine)copper(I) (IV) (1 655 g, yield 64 %) precipitated in 2 h Complex (IV), IR(KBr) ν(OCO, asym), 1550; ν(OCO, sym), 1413, δ(OCO, sym), 667 cm^{-1}. ^{1}H-NMR (C_6D_6) δ 2.36 (s, 3H, CH_3); δ 7 0 (m, 18H, m,p-phenyl); δ 7 6 (m, 12H, o-phenyl). From the reaction mixture trans-4-acetoxy-3-buten-2-one [13] was separated by means of gas chromatography (yield, 58 %) and characterized on the basis of its IR, NMR, and mass spectra, IR(CCl_4): ν(C=O) 1780, 1680 cm^{-1}. ^{1}H-NMR(CCl_4): δ 2 24 (s, 6H, methyl of acetyl and acetoxy group), δ 5.87 (d, 1H, J = 13Hz), δ 8.08 (d, 1H, J = 13Hz). mass spectrum (70eV) m/e, 128 (p).

Acetyl bromide (25 mg, 0 2 mmol) was added to complex II (135 mg, 0.2 mmol) in tetrahydrofuran (1 ml) and the reaction at room temperature for 1 h produced trans-4-acetoxy-3-buten-2-one (yield, 61 %).

2. Reaction of $CH_3Cu(PPh_3)_2 \cdot 0.5Et_2O$ (I) with isopropenyl acetate

Isopropenyl acetate (15 ml) was introduced into a Schlenk type flask containing I (3.84 g, 6 mmol) by trap-to-trap distillation. The initially yellow suspension gradually turned pale to give a white yellow precipitate (1.73 g) containing 2-acetoxy-1-propenylbis(triphenylphosphine)copper(I) (III) (m.p. 180°C with decomposition) and $CH_3COOCu(PPh_3)_2$ (IV) at -20 to -15°C in a day with evolution of methane (134.4 ml, S.T.P. 1.0 mol per copper). The product ratio of III to IV was determined as 4 : 3 by observing the ^1H-NMR spectrum of the crude product. Complex III was separated from the acetatocopper complex by fractional recrystallization of the precipitate from a mixture of tetrahydrofuran and diethyl ether. Complex III (Found: C, 71.4; H, 5.4; Cu, 9.1. $C_{41}H_{37}O_2Cu$ calcd.: C, 71.7, H, 5.4, Cu, 9.3 %). IR(KBr disc): ν(C=O) 1595 cm^{-1}. ^1H-NMR (C_6D_6): δ 2.00 (s, 6H, α-methyl and CH_3 of acetate), δ 5.42 (s, 1H, =CH); δ 7.0 (m, 18H, m,p-phenyl); δ 7.6 (m, 12H, o-phenyl)

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