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Preliminary communication

TRANSITION METAL-CATALYZED SYNTHESES OF ORGANIC ACIDS BY CHELATION-PROMOTED REGIOSELECTIVE DOUBLE BOND INSERTION

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Summary

The rhodium- or nickel-catalyzed reaction of vinylic halides with alkali salts of 3-butenoic acids leads to regioselective formation of dienoic acids, containing 3,5-conjugated double bonds. Monoarylacetylenes also react with 3-butenoic acids in a rhodium-catalyzed synthesis of the same acids. The stereochemistries of the acids and the nature of the by-products are discussed in the light of the proposed mechanisms.

In our programme aimed at devising new syntheses of linear unsaturated acids [1] we have been using the concept that, unlike simple olefins, a chelating ligand such as 3-butenoic acid should promote regioselective self-insertion into vinyl—rhodium or vinyl—nickel bonds, formed either by oxidative addition of vinyl halides to low-valent complexes of these metals or by protonation of coordinated alkynes.

We find that vinyl halides react with $Rh^{I}L_3Cl$ or $Ni^{0}L_{3-4}$ complexes (where L are trialkyl or triaryl phosphines, in part replaceable by olefins like 1,5-cyclooctadiene, COD) and under inert atmosphere with regioselective insertion of the double bond of 3-butenoic acids; the reaction is exemplified as follows for the reaction between β-bromostyrene and the potassium salt of 3-butenoic acid:

$$PhCH{=}CHBr + CH_2{=}CHCH_2COOK \xrightarrow{cat.} \underset{(I)}{PhCH{=}CHCH{=}CHCH_2COOH} + KBr$$

Two stereoisomers, 3-*E*-5-*E* and 3-*Z*-5-*E*, were formed in, approximately equal amounts, from *E*-β-bromostyrene (30 mmol), potassium 3-butenoate (30 mmol) and $RhCl(PPh_3)_3$ (0.1 mmol) in 27 ml of ethanol at 85°C for 48 h. Yield of

TABLE 1

^{1}H-NMR DATA FOR THE COMPOUNDS I, $Ph\overset{6}{C}H{=}\overset{5}{C}H\overset{4}{C}H{=}\overset{3}{C}H\overset{2}{C}H_2\overset{1}{C}OOH$, METHYL ESTERS[a]

Isomer	6-H	5-H	4-H	3-H	2-H	$J_{5,6}$	$J_{4,5}$	$J_{3,4}$	$J_{2,3}$
3-*Z*-5-*E*	3.40 d	3.025 dd	3.68 t	4.32 m	6.66 dd	15.44	10.29	11.03	7.35
3-*E*-5-*Z*	3.58 d	3.76 t	3.33 dd	4.07 qui	6.85 d	11.03	11.76	14.70	7.35
3-*Z*-5-*Z*	3.45 d	3.58 dd	3.35 t	4.27 m	6.69 dd	11.03	11.03	11.03	7.35
3-*E*-5-*E*	3.51 d	3.34 dd	3.71 dd	4.12 qui	6.83 dd	16.18	10.30	14.70	7.35

[a] At 270 MHz, τ,$CDCl_3$, J in Hz; s, singlet; d, doublet; t, triplet; q, quartet, qui, quintet; m, multiplet.

phenylhexadienoic acids 65%, 195 mol/mol of Rh complex. Refluxing the mixture with 10% KOH solution gave the known 3-*E*-5-*E* isomer [2]. *Z*-Styryl bromide did not react. With $Ni(PPh_3)_3$ (1 mmol) in place of the rhodium complex, *Z*-styryl bromide (10 mmol), potassium 3-butenoate (10 mmol), in 12 ml of ethanol at 85°C for 2 h, the 3-*E*-5-*Z* and 3-*Z*-5-*Z* stereoisomers were obtained in ca. 7 : 3 ratio (42% yield, the remainder being unchanged bromostyrene). The *E*-styryl bromide gave the 3-*Z*-5-*E* and 3-*E*-5-*E* stereoisomers in a 1 : 1 ratio (35% yield). Phenyl 5-*E*-hexenoic acid was also formed (6.4% yield).

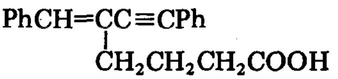
The stereoisomers could be separated by HPLC and GLC on capillary columns. Unequivocal NMR spectra of methyl esters (methylation with CH_2N_2) were recorded at 270 MHz (see Table 1).

The simplest representative of the 3,5-dienoic series, 3,5-hexadienoic acid, was obtained from vinyl bromide (20 mmol), potassium 3-butenoate (20 mmol) and $RhCl(PPh_3)_3$ (0.1 mmol) in 27 ml of ethanol at 85°C for 48 h. Saponification with 30% KOH solution gave sorbic acid (31% yield; 63 mol/mol of Rh complex).

Arylacetylenes were also examined as the source of the vinyl group. Ni^0 complexes were not effective, whereas Rh^I complexes were active catalysts. In this case all four 3,5-stereoisomers were present in comparable amounts. Thus the four isomers of I were obtained in the ratio 3-*E*-5-*Z* : 3-*Z*-5-*Z* : 3-*Z*-5-*E* : 3-*E*-5-*E* = 32 : 22 : 15 : 31 (elution order, SE 52 (polyphenylsilicone) glass capillary column) from phenylacetylene, (20 mmol), 3-butenoic acid (25 mmol), $RhCl(PPh_3)_3$ (0.2 mmol) and potassium 3-butenoate (15 mmol) at 85°C in 60 ml of 95% ethanol for 24 h; the yield of phenylhexadienoic acids was 45% based on the phenylacetylene taken (45 mol/mol of rhodium complex).

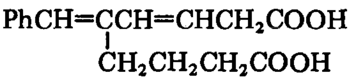
$$PhC{\equiv}CH + CH_2{=}CHCH_2COOH \xrightarrow{cat.} I$$

The following by-products were also isolated in the phenylacetylene reaction with $RhCl(PPh_3)_3$ (12, 3.5 and 0.3—0.5% yields based on phenylacetylene, respectively):



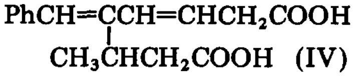
$$PhCH{=}\underset{\displaystyle CH_2CH_2CH_2COOH}{C}C{\equiv}CPh$$

(II)



$$PhCH{=}\underset{\displaystyle CH_2CH_2CH_2COOH}{C}CH{=}CHCH_2COOH$$

(III)



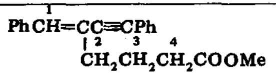
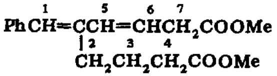
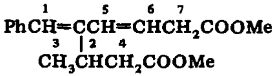
$$PhCH{=}\underset{\displaystyle CH_3CHCH_2COOH}{C}CH{=}CHCH_2COOH$$

(IV)

The configuration at the 3-double bonds in *E*. The configuration of the benzylidene groups was not ascertained.

TABLE 2

NMR DATA FOR THE COMPOUNDS II—IV, METHYL ESTERS [a]

	1	2	3	4	5	6	7	$J_{5,6}$	$J_{6,7}$
II  $\overset{1}{\text{PhCH}}{=}\text{CC}{\equiv}\text{CPh}$ $\overset{2}{\text{CH}_2}\overset{3}{\text{CH}_2}\overset{4}{\text{CH}_2}\text{COOMe}$	3.0 s [b]	7.48 t	7.95 qui	7.61 t					
III  $\overset{1}{\text{PhCH}}{=}\overset{5}{\text{CCH}}{=}\overset{6}{\text{CH}}\overset{7}{\text{CH}_2}\text{COOMe}$ $\overset{2}{\text{CH}_2}\overset{3}{\text{CH}_2}\overset{4}{\text{CH}_2}\text{COOMe}$	3.58 s	7.5—7.7 m	8.0—8.2 m	7.5—7.7 m	3.46 d	4.04 d	6.84 d	16	7
IV  $\overset{1}{\text{PhCH}}{=}\overset{5}{\text{CCH}}{=}\overset{6}{\text{CH}}\overset{7}{\text{CH}_2}\text{COOMe}$ $\overset{3}{\text{CH}_3}\overset{2}{\text{CH}}\overset{4}{\text{CH}_2}\text{COOMe}$	3.56 s	7.5—7.7 m	8.78 d	7.25 d 7.40 d	3.50 d	4.0 d	6.84 d	16	7

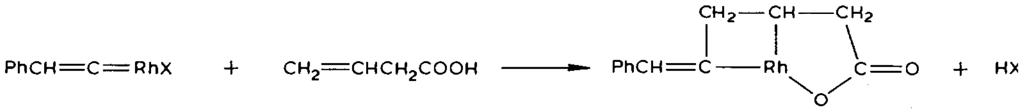
[a] At 270 MHz, τ, $CDCl_3$, J in Hz; s, singlet; d, doublet; t, triplet; q, quartet, qui, quintet; m, multiplet. [b] Hydrogenation gives a doublet at 7.05 τ.

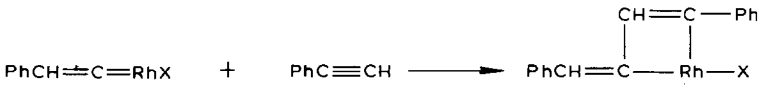
Another isomer of II (<1%) has M^+ 304 (methyl ester) and an ^{1}H NMR spectrum consistent with a double bond shift to the adjacent position. Very small amounts of two other isomers of II were also detected.

Selectivity towards the 3-*E*-5-*Z* isomer (ca. 75% of the phenylhexadienoic acids) was observed when a cationic Rh complex, $[Rh(COD)(PPh_3)_2]PF_6$, was used in the absence of potassium 3-butenoate and with addition of 4 mol of PPh_3 per mol of complex.

The difference in the stereochemistries of the compounds obtained from styryl bromide with Rh and Ni catalysts and those from phenylacetylene with Rh catalysts suggests that there are different intermediates. The presence of two stereoisomers in the former case involves stereospecific oxidative addition to the metal [3,4]. A non-stereospecific but regioselective insertion of butenoic acid follows, and β-hydrogen elimination gives the final product.

The stereochemistry of the phenylacetylene reaction does not seem to involve formation of styryl—metal bonds. Furthermore, the presence of benzylidene groups in the secondary products II—IV obtained from the reaction with $RhCl(PPh_3)_3$ may be attributed to the formation of a metal-bonded phenylvinylidene PhCH=C=RhX (X = Cl, Br, carboxylate) [5—7]. Subsequent insertion of an unsaturated molecule should lead to a four-membered metallacycle according to the metathesis mechanism [8—10] (phosphine ligands are omitted):





A formally internal hydrogen transfer would give rhodium phenylhexadienoate as precursor of free phenylhexadienoic acid, or 1,4-diphenylbutenine, which also is formed as a by-product. An insertion mechanism of this type was proposed by M.L.H. Green [11], but, to our knowledge has not been substantiated by experiments. Alternatively the four-membered ring could be enlarged by insertion of an alkyne or of a butenoic molecule before final H-transfer and ring opening to give compounds II—IV.

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