Journal of Organometallic Chemistry, 315 (1986) C45–C50
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

RHODIUM-CATALYZED C–C BOND FORMATION BY RING-OPENING OF ALKYLIDENECYCLOPROPANES AND INSERTION OF 3-BUTENOIC ACID

GIAN PAOLO CHIUSOLI, MIRCO COSTA, PAOLO SCHIANCHI
Istituto di Chimica Organica dell'Universita', Via Massimo D'Azeglio 85, 43100 Parma (Italy)

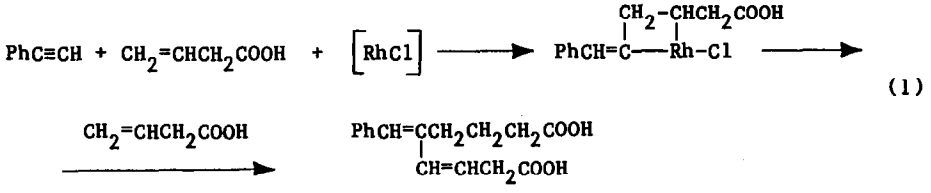
and GIUSEPPE SALERNO
Dipartimento di Chimica, Universita' della Calabria, I-87036 Arcavacata di Rende, Cosenza (Italy)

(Received July 24th, 1986)

Summary

Diphenylmethylenecyclopropane reacts with 3-butenoic acid in the presence of $RhCl(PPh_3)_3$ to give products resulting from insertion of one or two molecules of butenoic acid. Insertion of the first molecule of butenoic acid is not regioselective, whereas insertion of the second is highly regioselective.

We previously reported the formation of unsaturated acids by a rhodium-catalyzed regioselective reaction of dienes [1,2], allenes [3] and phenylacetylene [4] with 3-butenoic acids. In the latter case the presence of small amounts of dicarboxylic acids suggested the initial formation of rhodacycles followed by further insertion of butenoic acid (eq. 1, RhCl indicates the Rh complex):

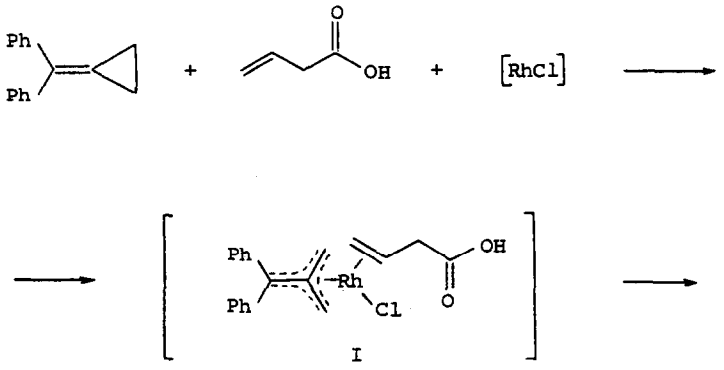


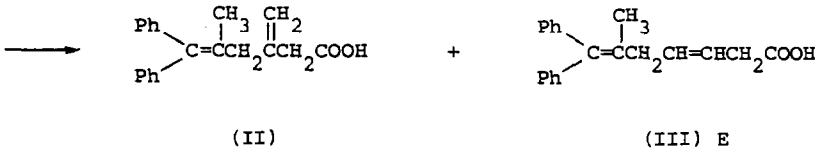
(1)

Since alkylidenecyclopropanes are known to react with transition metals by ring-opening and cycloaddition to various substrates [5,6], we wondered whether they could form open-chained compounds by reaction with 3-butenoic acid. We now have observed that diphenylmethylenecyclopropane [7] actually reacts with $RhCl(PPh)_3$ under mild conditions by ring-opening followed by insertion of 3-butenoic acid, to give mono- and di-basic unsaturated acids (eq. 2). Thus when

0022-328X/86/$03.50

diphenylmethylenecyclopropane, containing 1% mol of catalyst, was heated at 75°C in an excess of 3-butenoic acid used as solvent, the two monocarboxylic acids II and III (eq. 2) were obtained as the main products in 37 and 32% yields, respectively:

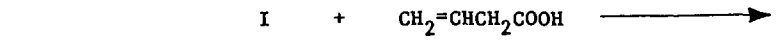




(II) (III) E

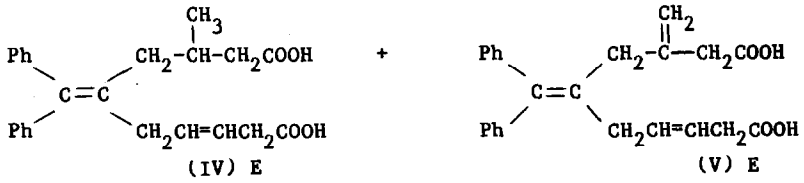
Other two dibasic acids (IV and V, ca. 1/1) were isolated in 6% yield (eq. 3).

Reaction 2 is not regioselective as far as the site of attack on the butenoic chain is concerned. In contrast, the previously described [1] reaction of butadiene (eq. 4) was found to be completely regioselective. This must be due to the fact that in reaction 2 the intermediate Rh complex I (containing a trimethylenemethane ligand, formally equivalent to a methylenerhodacyclobutane) cannot form the chelated ring (Cl replacement by COO is difficult) which is the prerequisite for the high regioselectivity obtained in reaction 4. In the latter reaction oxidative addition of butenoic acid to [RhCl] must first occur, whereas in reaction 2 the oxidative addition of the cyclopropane substrate must precede the reaction with butenoic acid.

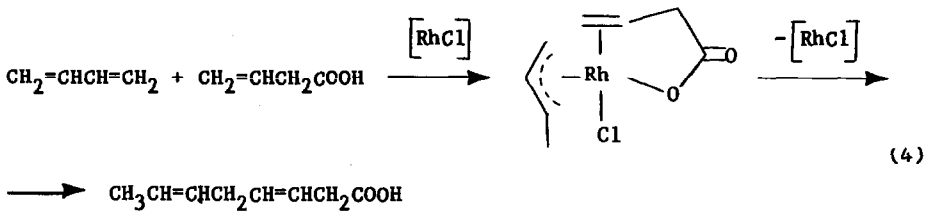


(3)

(2)

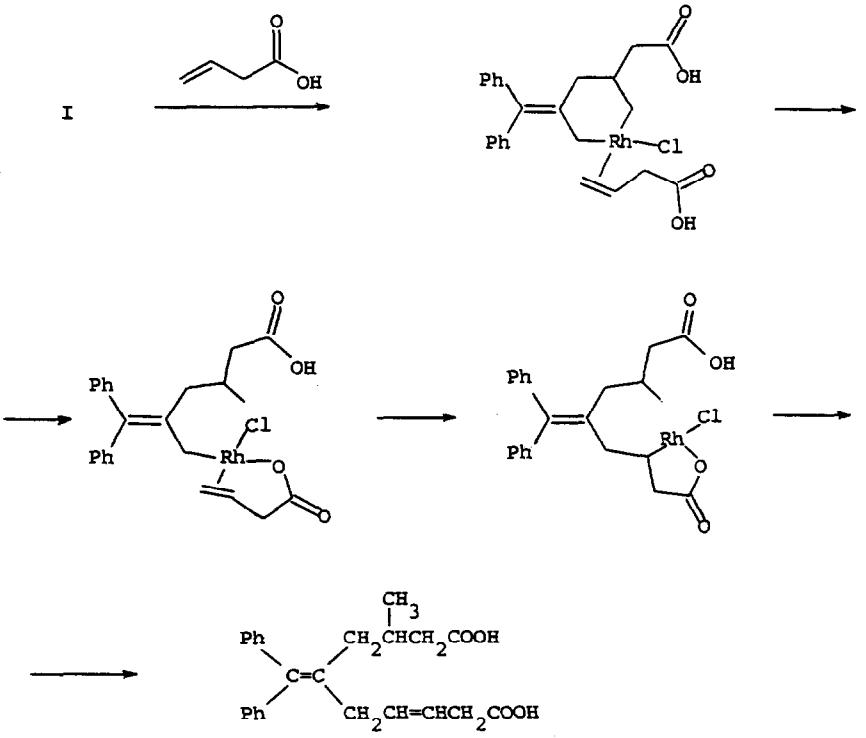


(IV) E (V) E



(4)

Further support for this interpretation comes from the formation of the dibasic acids (eq. 3). In this case the second molecule of butenoic acid can form a chelated ring and it inserts linearly. There is also a preference for the branched form of the butenoic group first inserted. Thus more than 90% of the dibasic acids contain one butenoic chain which has attached at the internal C atom of the double bond, whereas the other is derived from reaction at the terminal C atom. The insertion sequence can be depicted as follows (eq. 5):

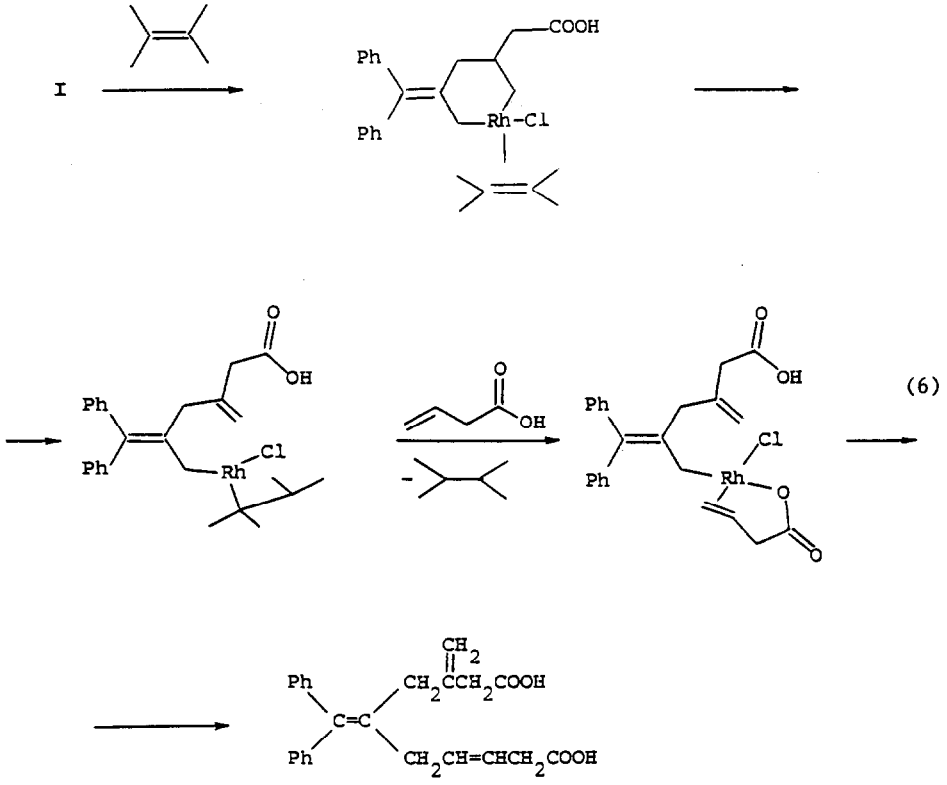


(5)

(IV) E

The preference for the branched butenoic chain in one of the butenoic units inserted must be due to an easier H-transfer within the complex containing the branched chain.

The same is true for the other dibasic acid which contains three double bonds, one of which is to the methylene group of the branched chain. The substrate or other unsaturated species generically denoted >=< compete with the Rh-bonded methylene group for H-transfer from the branched butenoic chain. In this way the branched monobasic acid is not formed and the chain remains attached to Rh until insertion of the second butenoic molecule takes place (eq. 6):



(V) E

The reaction of butenoic acid with alkylidenecyclopropanes has been found to be general. The site of ring-opening and the proportion of dicarboxylic acids formed varies, however, depending on the substrate.

These reactions offer a valuable route to compounds not easily accessible by other ways. Furthermore they offer new ways of using metallacycles in catalytic organic syntheses.

Experimental

The products were analyzed by GLC on a capillary OV 101 (methylsilicone) column with internal standard and separated by TLC (hexane/ethyl acetate 8/2 as eluent) and preparative HPLC on a reversed-phase n-C_{18} column using H_2O/MeOH as eluent.

Mass spectra were taken on a Finnigan 1020 Instrument (70 eV). ^1H and ^{13}C NMR spectra ($CDCl_3$ TMS internal standard) were recorded on a Bruker CXT 200 Instrument.

Physical data for the methyl esters of the isolated acids are reported below.

e d c b a f
$(Ph)_2C{=}C(CH_3)CH_2C(=CH_2)CH_2COOCH_3$ (II). MS: *m/e* 306 (M^+) 275, 232, 217, 191, 165, 115, 105, 91, 77, 59; IR (cm^{-1}): 3020, 2950, 1740, 1650, 1600, 1490, 1440, 1155, 1020, 900, 770, 700; ^1H NMR (δ): 3.00 (s, 2H, H_a); 5.02–5.06 (2s, 2H, H_b); 2.94 (s, 2H, H_c); 1.77 (s, 3H, H_d); 7.11–7.27 (m, 10H, H_e); 3.55 (s, 3H, H_f); ^{13}C NMR (δ): 171.2 (1C, CO), 143.4, 142.7, 140.8, 140.3, 131.3 (5 quaternary C), 129.4, (2C, =CH), 129.1, (2C, =CH), 127.9 (4C, =CH), 126.3 (2C, =CH) 114.9 (1C, $=CH_2$), 51.4 (1C, OCH_3), 42.4 (1C, CH_2), 41.5 (1C, CH_2), 19.7 (1C, CH_3). Ozonation products: $CH_3COCH_2COCH_2COOMe$, PhCOPh.

e d c b b a f
$(Ph)_2C{=}C(CH_3)CH_2CH{=}CHCH_2COOCH_3$ (III). MS: *m/e_1* 306 (M^+), 291, 274, 247, 232, 219, 191, 165, 115, 105, 91, 77, 59; IR (cm^{-1}): 3020, 2950, 1740, 1600, 1490, 1440, 1170, 970, 775, 700; ^1H NMR (δ): 3.08 (d, J_{ab} 5.0 Hz, 2H, H_a); 5.56–5.68 (m, 2H, H_b); 2.86 (m, 2H, H_c); 1.78 (s, 3H, H_d); 7.10–7.22 (m, 10H, H_e); 3.70 (s, 3H, H_f); ^{13}C NMR (δ): 172.5 (1C, CO), 143.0, 142.9, 139.0, 132.8 (4 quaternary C), 132.4 (1C, =CH), 129.5 (2C, =CH), 129.3 (2C, =CH), 127.9 (3C, =CH), 126.3 (2C, =CH), 126.1 (1C, =CH), 123.2 (1C, CH), 51.5 (1C, OCH_3), 38.8 (1C, CH_2), 37.8 (1C, CH_2), 19.6 (1C, CH_3). Ozonation products: $CH_2(COOMe)_2$, PhCOPh.

g d e f d i c b b a h
$CH_3OOCCH_2CH(CH_3)CH_2C(=CPh_2)CH_2CH{=}CHCH_2COOCH_3$ (IV). MS: *m/e* 406 (M^+), 374, 356, 332, 330, 287, 259, 231, 229, 205, 191, 167, 164, 115, 91, 77, 59; IR (cm^{-1}): 3020, 2950, 2920, 1740, 1600, 1490, 1440, 1260, 1165, 1010, 970, 740, 700; ^1H NMR (δ): 3.10 (m, 2H, H_a); 5.20 (m, 2H, H_b); 2.87 (m, 2H, H_c); 1.92–2.39 (m, 5H, $H_d + H_e$); 0.90 (d, J_{ef} 7.0 Hz, 3H, H_f); 7.08–7.30 (m, 10H, H_i); 3.70 (s, 3H, H_h); 3.64 (s, 3H, H_g). Ozonation product: $CH_2(COOMe)_2$, PhCOPh.

i d e f g c b b a h
$CH_3OOCCH_2C(=CH_2)CH_2C(=CPh_2)CH_2CH{=}CHCH_2COOCH_3$ (V). MS: *m/e* 404 (M^+), 372, 344, 341, 330, 243, 231, 229, 217, 167, 165, 115, 91, 77, 59; IR (cm^{-1}): 3060, 2960, 1740, 1650, 1600, 1490, 1435, 1270, 1170, 1015, 970, 900, 770, 740, 700; ^1H NMR (δ): 3.06 (d, J_{ab} 4.3 Hz, 2H, H_a); 5.48–5.54 (m, 2H, H_b); 2.85 (m, 2H, H_c); 2.99 (s, 2H, H_d); 5.08 (s, 2H, H_e); 2.92 (s, 2H, H_f); 7.12–7.40 (m, 10H, H_g); 3.70 (s, 3H, H_h); 3.56 (s, 3H, H_i). Ozonation products: $CH_2(COOMe)_2$, PhCOPh.

Acknowledgement This work was supported by Ministero della Pubblica Istruzione.

References

1 G.P. Chiusoli, L. Pallini, and G. Salerno, J. Organomet. Chem., 238 (1982) C85.
2 G. Salerno, F. Gigliotti, and G.P. Chiusoli, J. Organomet. Chem., 314 (1986) 231.
3 G. Salerno, G. Gallo, G.P. Chiusoli, and M. Costa, J. Organomet. Chem., submitted.
4 G.P. Chiusoli, G. Salerno, W. Giroldini, and L. Pallini, J. Organomet. Chem., 219 (1981) C16.
5 B.M. Trost, Angew. Chem. Int. Ed. Engl., 25 (1986) 1.
6 P. Binger, M. Cetinkaya, M.J. Doyle, A. Germer, and U. Schuchardt, Fund. Res. Hom. Catal., 3 (1979) 271.
7 K. Sisido, K. Utimoto, Tetrahedron Lett., (1966) 3267.