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Rhodium-catalyzed C–C coupling reactions involving ring opening of strained molecules

II *. Addition to olefins and aromatic substitution

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Abstract

Rhodium-catalyzed C–C coupling reactions, involving ring opening of strained molecules, have been studied using diphenylmethylenecyclopropanes as models. It has been established that, as rhodium takes control of the ring opening process, activated olefins can react to form open-chain unsaturated compounds. In the presence of acids, protonation of the substrate competes with olefin incorporation, and intramolecular aromatic electrophilic substitution, leading to indene derivatives, can be obtained. Aromatic substitution can also occur in a sequential process, involving ring opening, 3-butenoic acid addition, leading to linear and branched isomeric complexes, and selective formation of a benzocycloheptene derivative from the branched isomer. The regioselectivity of 3-butenoic acid insertion is contrasted with the non-regioselectivity observed with the same acid in reactions which probably involve metallacycle formation.

Introduction

In the course of our studies aimed at investigating the reactivity of metallacyclobutane or trimethylenemethane-type intermediates, formed in situ from unsaturated compounds [1], we observed that (diphenylmethylene)cyclopropane (I) reacts with 3-butenoic acid as solvent to give mainly unsaturated acids (III and IIIa, eq. 1, Y = CH_2COOH). Further development of this reaction allowed us to uncover new aspects, connected with the reactivity of activated olefins and with competitive or sequential aromatic substitution. These and related aspects are reported here.

* For part I see ref. 1.

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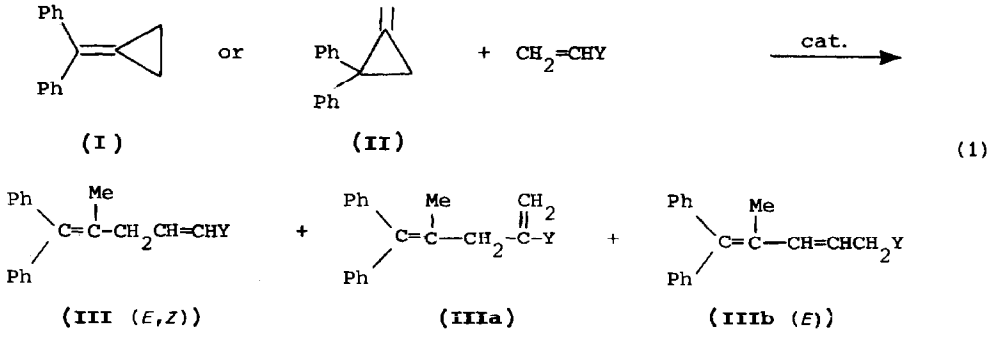
Results

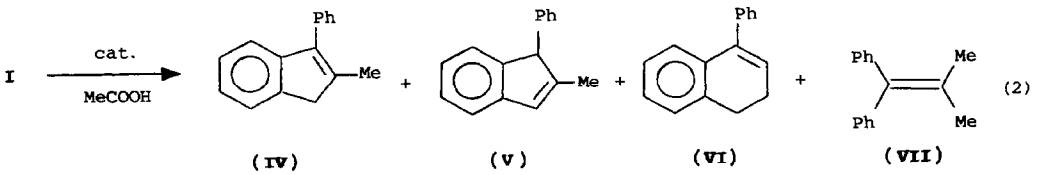
We distinguish two types of olefinic reagents: (a) activated olefins; (b) unsaturated acids.

(a) Activated olefins. Working with $RhCl(PPh_3)_3$ as catalyst at 90 °C in toluene as solvent, we observed the following reaction (eq. 1, Y = COOEt, CN, Ph), leading only to III and IIIb in yields (based on I or II) of 75 to 97% at complete conversion:

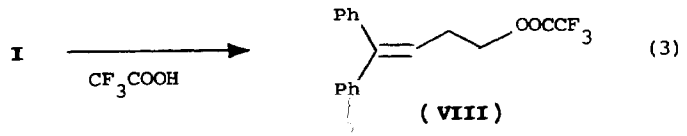


Thus I, Y = COOEt, gave III (*E*) 75% (other isomers 16%); II, Y = COOEt, gave III (*E*) 70% (76% conversion); I, Y = CN, gave III (*E*) 14%, III (*Z*) 14%, IIIb (*E*) 64% and I, Y = Ph, gave III (*E*) 97%. A substrate (I or II) to catalyst molar ratio of 50 was adopted for all the experiments, and no attempts were made to optimize catalytic efficiency and selectivity.

In the presence of a small amount of a saturated carboxylic acid such as acetic acid the reaction took a completely different course, even in the presence of activated olefins. Thus substrate I gave the indene derivative IV as the major product (77% yield), together with its isomer V (4%), phenyldihydronaphthalene VI [2] (4%), and diphenylmethylpropene VII [3] (8%) (eq. 2):



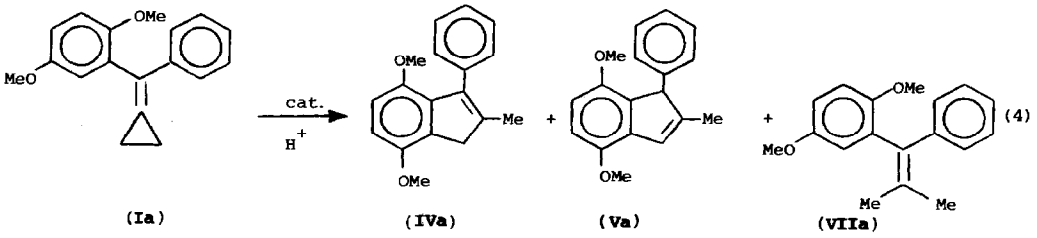
The behaviour of acetic acid in the absence of the rhodium catalyst was examined, and no reaction observed. In contrast, trifluoroacetic acid gave VIII, as previously reported [4] (eq. 3):



We also found that acids stronger than acetic acid, such as cyanoacetic acid, behave analogously (90% yield of $(Ph)_2C{=}CHCH_2CH_2OOCCH_2CN$ (VIIIa)). Under the same conditions, 1,1-diphenylbutadiene (IX), a possible intermediate, did not react.

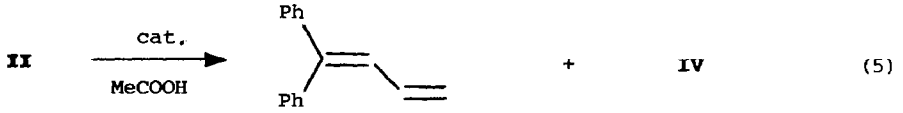
The formation of indene derivatives appears to be highly selective. The dimethoxy derivative of I, in which phenyl and dimethoxyphenyl groups are in

competition (Ia), underwent ring closure exclusively on the aromatic ring bearing the substituents (eq. 4). Product IVa predominated (75%). Minor amounts of isolated compounds derived from double bond shift (Va) and hydrogenolysis (VIIa).



(Ia) (IVa) (Va) (VIIa)

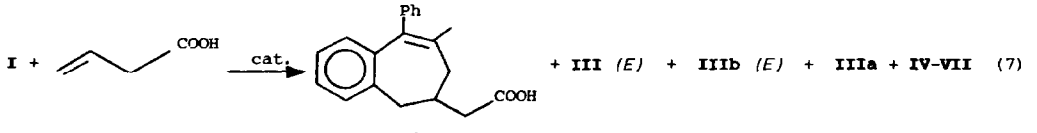
Compound II reacted with activated olefins in the same way as its isomer I, but gave 1,1-diphenylbutadiene IX (84%) and IV (5%) in the presence of added acetic acid, under the same conditions that led to conversion of I into IV (eq. 5). No reaction occurred in the absence of the catalyst. Compound II with trifluoroacetic acid, both in the presence and in the absence of the rhodium catalyst, gave IV (eq. 6) quantitatively. Compounds V–VII were not formed, however.



(IX)

Other acids stronger than acetic approach trifluoracetic acid in behaviour, giving increasing amounts of IV as the acid strength increases.

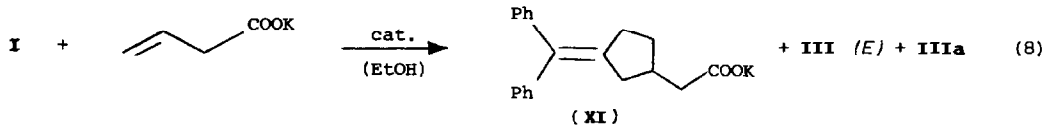
(b) Unsaturated acids. When 3-butenoic acid in toluene was used under the conditions described above, substrate I gave III (*E*) (25%), IIIb (*E*) (21%), IIIa (3%) (eq. 1, Y = CH_2COOH) and a new product (X, 31%), containing a benzocycloheptene ring (eq. 7):



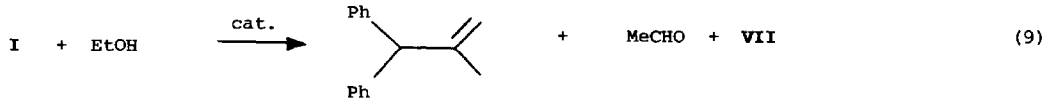
(X)

Because of the acidity of the medium (eq. 2) compounds IV–VII were also formed (12%). Compound X is derived from the skeleton of the branched isomer IIIa, but under the same conditions the latter was not converted into X, even in the presence of trifluoroacetic acid.

Substrate I was also used with potassium 3-butenoate in ethanol as solvent. Compounds III (*E*) (25%), and IIIa (15%) were obtained, but the product resulting from the known [5] 3 + 2 cycloaddition, XI (26%) was also formed (eq. 8). In addition compound VIIb [6] (20%) was present. The latter is derived from hydrogenolysis at the expense of ethanol, as shown by an experiment carried out in the absence of potassium butenoate (eq. 9) (54% yield of VIIb and 37% of VII).

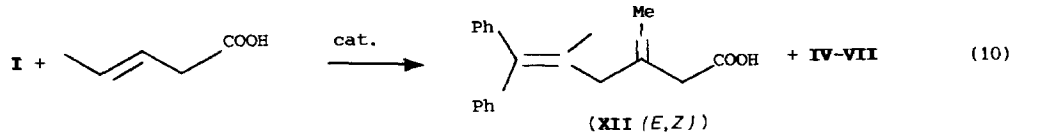


(XI)



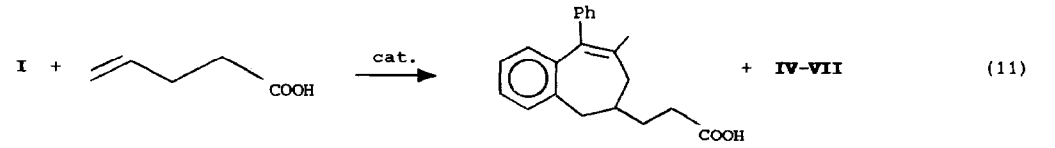
(VIIb)

If unsaturated acids other than 3-butenoic are used, yields of addition products drop to low values, and IV–VII are formed predominantly. Thus 3-pentenoic acid gave XII (*E*,*Z*) (15%) and IV–VII (85%) (eq. 10).



(XII (*E*,*Z*))

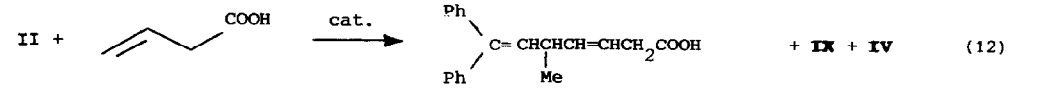
With 4-pentenoic acid only a 25% yield of an acid mixture was obtained (eq. 11), containing XIII and open-chained isomers in a 2/3 ratio. The neutral part (IV–VII) accounted for 75%.



(XIII)

No significant reaction of the double bond was observed with esters of 3-butenoic and of 3 and 4-pentenoic acids or with simple olefins.

Compound II did not react directly with 3-butenoic acid, but isomerized to 1,1-diphenylbutadiene (IX), in accord with the behaviour observed in the presence of weak acids (eq. 5). Insertion of butenoic acid into the allylrhodium complex formed from IX (see Discussion) slowly followed, and gave XIV (*E*) (19%), XIV (*Z*) (12%), IX (55%) and IV (5%) (eq. 12). Compounds XIV were also obtained starting from IX, thus confirming that they are formed by a ring opening process different from that observed for substrate I. As expected for an insertion reaction, the butenoic chain is inserted linearly.

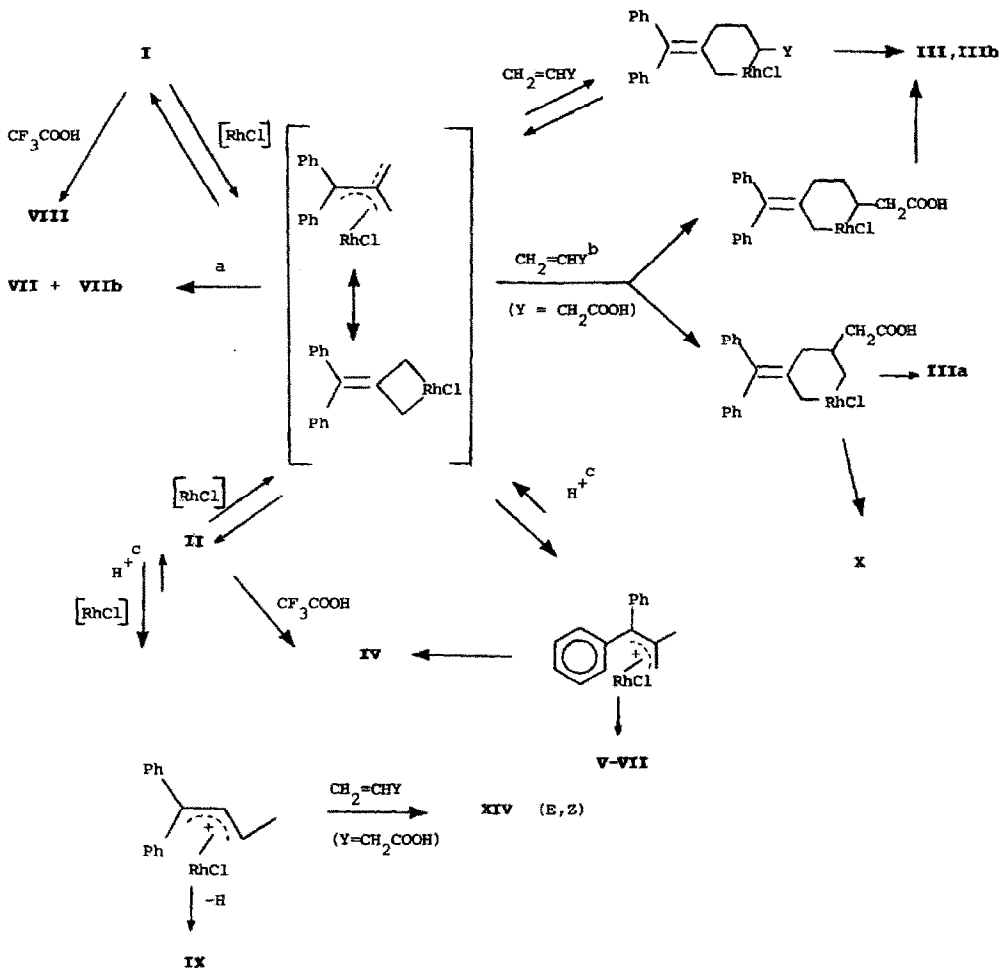


(XIV (*E*,*Z*))

Discussion

The reaction of I and II can be rationalized according to Scheme 1 (in which ligands not relevant to understanding of the reactions are omitted).

Ring closure to IV clearly is an electrophilic process, as shown by the outcome of

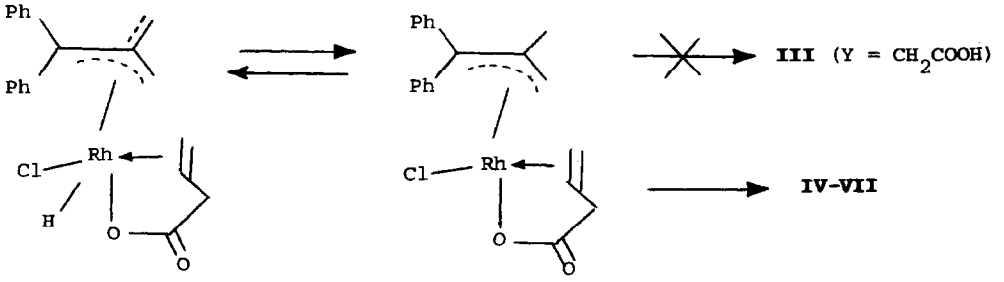


Scheme 1. (a) in ethanol, substrate I; (b) substrate I, (c) acetic acids or weak acids.

the competition experiment between a dimethoxy-substituted and an unsubstituted phenyl ring, which led to ring closure exclusively at the substituted one. Protonation can, however, give rise to different electrophilic species, depending on the acid strength, as shown by the different behaviours of acetic and trifluoroacetic acid. The presence of the rhodium complex can stabilize one of the intermediates if the metal takes control of the ring opening process before protonation or in the absence of an efficient protonation (for literature on the various ring opening processes see ref. 5 and 7). A strong acid such as trifluoroacetic is able to protonate the substrate before the intervention of the rhodium complex, and the reaction leads to VIII in the case of I, and to IV in the case of II. With a weaker acid, such as acetic acid, the formation and protonation of the trimethylenemethane [7] species must be controlled by the rhodium complex. This was clearly indicated by the fact that when the protonated precursor of IV is formed in the absence of rhodium (from substrate II) only IV is formed, and not V–VII, which are derived from rhodium-promoted double bond isomerization, skeletal isomerization, and hydrogenolysis (these secondary reactions, although new for this type of substrates, will not be considered

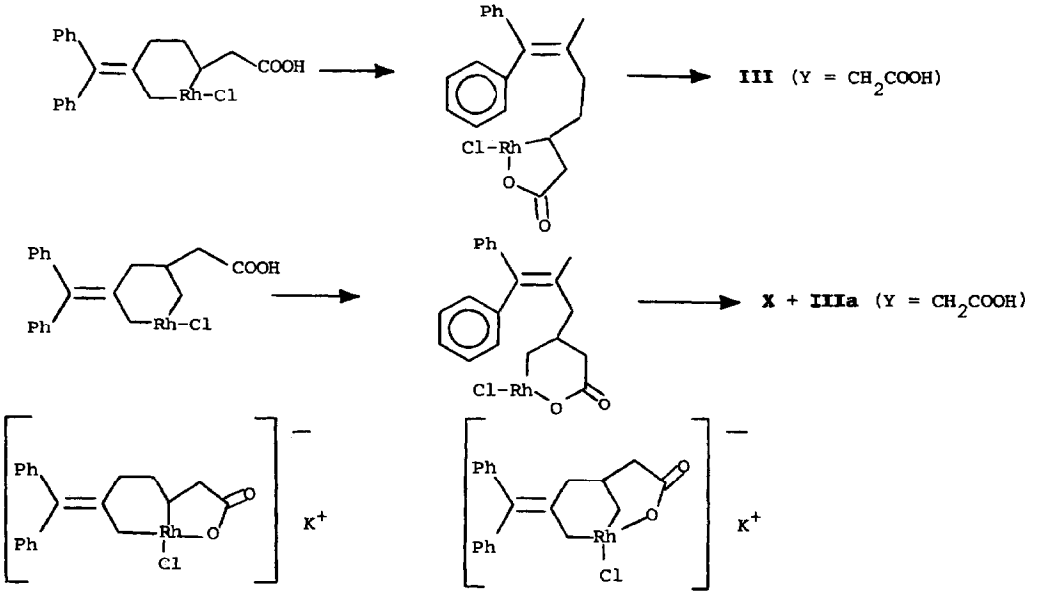
here). Substrate II, which with activated olefins afforded the same products as I (eq. 1), shows a completely different behaviour in the presence of acids (eq. 5 and 12).

The postulated formation of the metallacycle precursors of III and IIIa from the trimethylenemethane species and olefins is straightforward. Contrary to what is generally observed with Ni and Pd [5], the 3 + 2 cycloaddition does not take place, except in the case of the potassium salt of butenoic acid, and the metallacycle undergoes hydrogen transfer from the alkyl chain to the C–Rh bond. In the case of Y = CH_2COOH, chelation occurring via oxidative addition of the acid to rhodium might be suggested in view of the fact that the methyl ester, as well as simple olefins, are not sufficiently strongly coordinating to undergo reaction (Scheme 2). If this



Scheme 2

were the case, however, we would expect formation of an allyl complex (by H-addition to the trimethylenemethane group), which besides giving IV, should insert the double bond of the chelating ring regioselectively [8]; an example is offered by the regioselective reaction of diphenylbutadiene IX with butenoic acid (eq. 12). In contrast we observe a non-regioselective reaction, and therefore conclude that what is involved is not an insertion (migration of a metal-bonded group to an unsaturated molecule) but a reversible metallacycle formation (Scheme 1)



Scheme 3

from two coordinated molecules (trimethylenemethane and butenoic acid). The role of the acid would be that of providing an irreversible step by protonolysis of the C–Rh bond and formation of a rhodium-chelated ring (Scheme 3). The fact that the reaction also proceeds with potassium butenoate seems to indicate that some kind of chelation, possibly giving rise to an anionic rhodium complex as shown in Scheme 3, stabilizes the intermediate.

The rhodium-bonded precursor of IIIa (Scheme 3) must possess sufficiently good electrophilic properties to be able to attack the aromatic ring to form X. The shift from H-elimination (leading to IIIa) to aromatic substitution to form X seems to occur when a sterically unhindered primary alkyl group is bonded to rhodium. Thus only the branched chain precursor of IIIa (and not of III) leads to X. As a consequence the benzocycloheptene ring formation turns out to be a highly chemo- and regio-selective reaction.

Summing up, our work has shown that:

(1) Labile intermediates, such as trimethylenemethane derivatives, when trapped by rhodium complexes, can be induced to form open-chained products by addition to activated or chelating olefins. In the presence of acids, intramolecular aromatic substitution can occur, depending on competition between protonation and metallacycle formation.

(2) Sequential olefin addition and aromatic substitution to form a seven-membered ring can also be achieved under the control of the metal center, which is able to form the appropriate electrophilic species in a highly selective way.

(3) Metallacycle formation has different requirements from the olefin insertion reaction, as shown by the very different regiochemistry observed in the reaction of (diphenylmethylene)cyclopropane and diphenylbutadiene with butenoic acid.

Experimental

Products were analyzed and quantitatively determined by GLC on a methyl silicone (OV-101 stationary phase) capillary column with internal standard, and isolated by HPLC or preparative flash chromatography under nitrogen (1 atm). Compounds were identified by comparison with authentic samples or by mass and NMR spectra. Mass spectra were recorded on a Finnigan 1020 instrument at 70 eV. ^{1}H NMR and ^{13}C NMR spectra were recorded with AC100, AC300 and CXP200 Bruker spectrometers; chemical shifts are in ppm (δ) from TMS as reference.

The starting complex $RhCl(PPh_3)_3$ [9] and some materials ((diphenylmethylene)-cyclopropane (I) [10], (diphenyl)methylenecyclopropane (II) (Pinhas et al. [7]), 1,1-diphenylbutadiene (IX) [11]) were prepared by published methods.

1-Phenyl-1-(2′,5′-dimethoxyphenyl)methylenecyclopropane (Ia) was prepared by the procedure used for compound I, starting from 2,5-dimethoxybenzophenone (obtained by Friedel–Crafts reaction of *p*-dimethoxybenzene with benzoyl chloride) instead of benzophenone. Ia was purified by flash chromatography on silica gel with n-hexane/ethyl acetate 95/5 as eluent. Yellow solid (m.p. 44°C). ^{1}H NMR, ($CDCl_3$), δ 1.14–1.26, m, 2H, CH_2; 1.53–1.68, m, 2H, CH_2; 3.60, s, 3H, OMe; 3.78, s, 3H, OMe; 6.8–6.9 m, 3H, substituted Ph, 7.17–7.50, m, 5H, unsubstituted Ph. Mass spectrum: *m/e*: 266 (M^+), 251, 236, 235 (base), 220, 204, 191, 189, 178, 165, 152, 115, 77.

The general procedure adopted for activated olefins is reported below (a). It was slightly modified for saturated (b) and unsaturated (c) organic acids.

(a) In a Schlenk tube 0.02 g (0.02 mmol) of catalyst, 1 mmol of substrate I (or II) and 3 mmol of activated olefin were dissolved in 3 ml of toluene under nitrogen (eq. 1). The solution was stirred magnetically at 90 °C for 60 h and products were separated by chromatography.

III (*E*) (Y = Ph) was isolated by flash chromatography on silica gel with n-hexane as eluent; III (*E*) (Y = COOEt) by the same technique with n-hexane/ethyl acetate 95/5 as eluent; III (*E*,*Z*), Y = CN and IIIb (*E*) Y = CN by HPLC on a reverse phase C-18 column using MeOH/H_2O 82/18 as eluent. The same procedure and the same quantities of reagents were used with the potassium salt of 3-butenoic acid instead of the activated olefin in EtOH (5 ml) (eq. 8).

The acid products (III (*E*), IIIa and XI) were separated from the reaction mixture and converted into the respective methyl esters, which were purified by HPLC on a reverse phase C-18 column, using MeOH/H_2O 8/2 as eluent. Ozonation of the methyl ester of compound XI gave benzophenone and 3-oxocyclopentaneacetic acid methyl ester [12].

Under the same conditions, 0.02 g (0.02 mmol) of catalyst and 1.0 mmol of substrate I were caused to react in 3 ml of EtOH (eq. 9). Products VII and VIIb were isolated by HPLC on a silica gel column using n-hexane as eluent.

(b) Under the conditions described in (a), 0.02 g (0.02 mmol) of catalyst, 1 mmol of substrate I or Ia and 0.16 mmol of a saturated organic acid (e.g. acetic acid) were allowed to react in 3 ml of toluene (eq. 2 and 4). Products V–VII were isolated by HPLC on silica gel column using n-hexane as eluent, and products IVa, Va and VIIa by HPLC reverse phase C-18 column with MeOH/H_2O 67/33 as eluent.

Substrate II required a larger amount of acid than I: 0.02 g (0.02 mmol) of catalyst, 10 mmol of substrate II, 5.0 mmol MeCOOH and 3 ml of toluene were used (eq. 5), and products IX and IV were separated by flash chromatography on silica gel with n-hexane as eluent. Product IX was characterized by comparison with literature data [11].

Reactions without catalyst (eq. 3 and 6) were carried out in the same way using 1 mmol of substrate (I or II), and 3 mmol of acid in 3 ml of toluene. Product VIIIa was isolated by flash chromatography on silica gel with n-hexane/ethyl acetate 9/1.

(c) Under the same conditions as in (a) 0.02 g (0.02 mmol) of catalyst, 1.0 mmol of substrate I or II and 5 mmol of unsaturated acid (10 mmol with substrate II) were allowed to react in 2 ml of toluene (eq. 7, 10, 11 and 12). After the usual treatment the methyl esters of the acid products were isolated by HPLC using a reverse phase C-18 column with MeOH/H_2O 8/2 as eluent. The methods used for separation of the neutral products were as in (b).

Properties of new compounds (acids were converted to methyl esters for characterization; NMR spectra were recorded for $CDCl_3$ solutions unless otherwise indicated)

III (*E*), Y = COOEt. MS: (*m/e*): 306 (M^+), 277, 264 (base), 233, 218, 203, 191, 178, 165, 152, 139, 128, 115, 91, 77. ^{1}H NMR: δ 1.31, t, 3H, *J* 7.0 Hz, Me; 1.79 s, 3H, Me; 3.0, dd, 2H, *J* 6.6 Hz, *J* 1.6 Hz, CH_2; 4.20, q, 2H, *J* 7.0 Hz, OCH_2; 5.84, dt, 1H, *J* 15.6, *J* 1.6 Hz, =CH; 7.0, dt, 1H, *J* 15.6 Hz, *J* 6.6 Hz, =CH; 7.10–7.35, m, 10 H, 2Ph.

III (*E*), Y = CN. MS: (*m/e*): 259 (M^+), 244 (base), 217, 204, 191, 182, 165, 115, 91, 77. ^{1}H NMR: δ 1.78, s, 3H, Me; 3.05; dd, 2H, *J* 6.6 Hz, *J* 1.8 Hz, CH_2; 5.32, dt, 1H, *J* 16.3 Hz, *J* 1.8 Hz, =CH; 6.75, dt, 1H, *J* 16.3 Hz, *J* 6.6 Hz, =CH; 7.07–7.36, m, 10H, 2Ph.

III (*Z*), Y = CN. MS: (*m/e*): 259 (M^+, base), 244, 217, 204, 190, 182, 165, 115, 91, 77. ^{1}H NMR: δ 1.80, s, 3H, Me; 3.24, dd, 2H, *J* 7.6 Hz, *J* 1.4 Hz, CH_2; 5.37, dt, 1H, *J* 10.8 Hz, *J* 1.4 Hz, =CH; 6.45, dt, 1H, *J* 10.8 Hz, *J* 7.6 Hz, =CH; 7.10–7.37, m, 10H, 2Ph.

IIIb (*E*), Y = CN. MS: (*m/e*): 259 (M^+), 219 (base), 204, 165, 141, 115, 91, 77. ^{1}H NMR: δ 1.93, s, 3H, Me; 3.14, dd, 2H, *J* 6.2 Hz, *J* 1.2 Hz, CH_2; 5.65, dt, 1H, *J* 15.5 Hz, *J* 6.2 Hz, =CH; 6.6, dt, 1H, *J* 15.5 Hz, *J* 1.2 Hz, =CH; 7.10–7.33, m, 10H, 2Ph.

III (*E*), Y = Ph. MS: (*m/e*): 310 (M^+), 219 (base), 204, 191, 165, 115, 91, 77. ^{1}H NMR: δ 1.82, s, 3H, Me; 3.00, d, 2H, *J* 6.5 Hz, CH_2; 6.20, dt, 1H, *J* 16.0 Hz, *J* 6.5 Hz, =CH; 6.40, d, 1H, *J* 16.0 Hz, =CH; 7.10–7.36, m, 15H, 3Ph.

III (*E*), Y = CH_2COOMe. MS: (*m/e*): 306 (M^+), 291, 274, 246, 232, 219 (base), 217, 204, 191, 165, 115, 91, 77, 59. ^{1}H NMR: (C_6D_6): δ 1.75, s, 3H, Me; 2.79, m, 2H, CH_2; 2.85, m, 2H, CH_2CO; 3.32, s, 3H, OMe; 5.44, dtt, 1H, *J* 15.3 Hz, *J* 8.0 Hz, *J* 1.0 Hz, =CH; 5.6, dtt, 1H, *J* 15.3 Hz, *J* 8.3 Hz, *J* 1.0 Hz, =CH; 7.02–7.28, m, 10H, 2Ph.

IIIa, Y = CH_2COOMe. MS: (*m/e*): 306 (M^+), 275, 232 (base), 217, 191, 165, 115, 105, 91, 77, 59. ^{1}H NMR: δ 1.77, s, 3H, Me; 2.94, s, 2H, CH_2; 3.0, s, 2H, CH_2CO; 3.57, s, 3H, OMe; 5.03, brs, 2H, $=CH_2$; 7.19–7.32, m, 10H, 2Ph.

IIIb (E), Y = CH_2COOMe. MS: (*m/e*): 306 (M^+), 275, 264, 246, 232, 219 (base), 217, 204, 191, 178, 165, 155, 141, 128, 115, 105, 91, 77, 59. ^{1}H NMR: δ 1.9, s, 3H, Me; 2.37; s, 2H, CH_2; 2.39, d, 2H, *J* 3.0 Hz, allylic CH_2; 3.65, s, 3H, OMe; 5.81, dt, 1H, *J* 15.5 Hz, *J* 3.0 Hz, =CH; 6.38, d, 1H, *J* 15.5 Hz, =CH; 7.09–7.40, m, 10H, 2Ph. Hydrogenated IIIb MS: (*m/e*): 310 (M^+), 219, 195, 167 (base), 165, 152, 143, 111, 83, 69, 55.

IV. MS: (*m/e*): 206 (M^+, base), 191, 189, 165, 128, 101, 91, 77, 76. ^{1}H NMR: δ 2.14, s, 3H, Me; 3.45, s, 2H, CH_2; 7.10–7.25, m, 4H, aromatics; 7.30–7.45, m, 5H, Ph. ^{13}C NMR: δ 146, 142, 141(2), 136, (quaternary C); 129(2), 128, 127, 126, 124, 123, 119(2), (=CH); 43.1, CH_2; 15.1, (Me).

IVa. MS: (*m/e*): 266 (M^+, base), 251, 236, 235, 208, 178, 165, 115, 89, 76. ^{1}H NMR: δ 2.05, s, 3H, Me; 3.47, s, 2H, CH_2; 3.72, s, 3H, OMe; 3.79, s, 3H, OMe; 6.83–6.95, m, 2H, substituted aromatic; 7.04–7.46, m, 5H, unsubstituted aromatic.

V. MS: (*m/e*): 206 (M^+, base), 191, 189, 165, 128, 91, 77, 76. ^{1}H NMR: δ 1.89, br s, 3H, Me; 4.27, br s, 1H, CH; 6.52, br s, 1H, =CH; 7.01–7.40, m, 9H, aromatics.

Va. MS (*m/e*): 266 (M^+, base), 251, 236, 235, 208, 191, 189, 178, 165, 152, 115, 91, 77, 63. ^{1}H NMR: δ 1.86, br s, 3H, Me; 3.54, s, 3H, OMe; 3.86, s, 3H, OMe; 4.38, br s, 1H, CH; 6.6, br s, 1H, =CH; 6.68–6.80, m 2H, substituted aromatic; 7.00–7.26, m, 5H, unsubstituted aromatic.

VIIa. MS: (*m/e*); 268 (M^+, base), 253, 237, 223, 195, 178, 165, 152, 129, 115, 105, 91, 77, 63. ^{1}H NMR: δ 1.68, s, 3H, Me; 1.82, s, 3H, Me; 3.64, s, 3H, OMe; 3.75, s, 3H, OMe; 6.68–6.80, m, 3H, substituted aromatic; 7.05–7.27, m, 5H, unsubstituted aromatic.

VIIIa. MS: (*m/e*): 291 (M^+), 206 (base), 191, 178, 165, 128, 115, 91, 77, 68. ^{1}H NMR: δ 2.50, dt, 2H, *J* 7.4 Hz, *J* 6.7 Hz, allylic CH_2; 3.41, s, 2H, CH_2; 4.26, t, 2H, *J* 6.7 Hz, OCH_2; 6.04, t, 1H, *J* 7.4 Hz, =CH; 7.12–7.42, m, 10H, 2Ph.

X, Methyl ester. MS: (*m/e*): 306 (M^+), 291, 274, 264, 246, 232 (base), 219, 217, 204, 191, 178, 165, 155, 141, 129, 115, 91, 77, 59. ^{1}H NMR: (C_6D_6), δ 1.66, dd, 1H, J_{gem} 12.6 Hz, *J* 8.34 Hz, allylic CH; 1.82, s, 3H, Me; 1.94, dd, 1H, J_{gem} 12.6 Hz, *J*

5.8 Hz, allylic CH; 2.08, dd, 1H, J_{gem} 15.0 Hz, J 6.7 Hz, exocyclic CH; 2.26, dd, 1H, J_{gem} 15.0 Hz, J 7.8 Hz, exocyclic CH; 2.43, dd, 1H, J_{gem} 12.0 Hz, J 4.0 Hz, benzylic CH; 2.8–3.0, m, 2H, benzylic CH and asymmetric CH; 3.44, s, 3H OMe; 7.32–7.66, m, 9H aromatics. The homonuclear ^{1}H (300.133 MHz) 2D-COSY spectrum allows to distinguish between the assigned structure and an alternative one, possibly deriving from III (Y = CH_2COOH), on the ground that only structure X contains a proton which is coupled with other six. Hydrogenation revealed one unsaturation and led to only one of the two possible diastereoisomers. Hydrogenated X, MS: (*m/e*): 308 (M^+), 276, 248, 234, 219, 217, 205, 192, 179, 165, 143, 127 (base), 115, 105, 91, 77, 59. On ozonation X gave a product, the molecular weight of which corresponded to the uptake of two oxygen atoms as expected for PhCO(*o*-C_6H_4)CH_2CH(CH_2COOMe)CH_2COMe. MS: (*m/e*): 338 (M^+) 282, 281 (base), 277, 263, 249, 231, 221, 208, 207, 206, 205, 204, 203, 196, 195, 194, 178, 165, 115, 105, 91, 77, 43.

XII (*E*), Methyl ester. MS: (*m/e*): 320 (M^+), 288, 261, 246, 233 (base), 218, 205, 191, 165, 115, 105, 91, 77, 59. ^{1}H NMR: δ 1.6, d, 3H, J 7.2 Hz, Me; 1.7, s, 3H, Me; 2.86, s, 2H, CH_2; 3.06, s, 2H, CH_2CO; 3.69, s, 3H, OMe; 5.36, q, 1H, J 7.2 Hz, =CH; 7.13–7.36, m, 10H, 2Ph.

XII (*Z*); methyl ester. MS: (*m/e*): 320 (M^+, absent), 288, 246, 233 (base), 205, 192, 191, 167, 165, 115, 95, 77, 59. ^{1}H NMR: δ 1.6, d, 3H, J 7.2 Hz, Me; 1.7, s, 3H, Me; 2.76, s, 2H, CH_2; 3.13, s, 2H, CH_2CO; 3.68, s, 3H, OMe; 5.35, q, 1H, J 7.2 Hz, =CH; 7.13–7.36, m, 10H, 2Ph.

XIII, methyl ester. MS: (*m/e*): 320 (M^+), 278, 259, 246, 233, 231, 217, 204 (base), 191, 178, 165, 155, 141, 128, 115, 105, 91, 77, 59. ^{1}H NMR (C_6D_6): δ 1.53–1.70, m, 2H, exocyclic CH_2; 1.85, s, 3H, Me; 1.89–1.95, m, 2H, allylic CH_2; 2.21, t, 2H, J 8.0 Hz, CH_2CO; 2.28–2.34, m, 2H, asymmetric CH, benzylic CH; 2.76, dd, 1H, J 12.2 Hz, J 6.33 Hz, benzylic CH; 3.45, s, 3H, OMe; 6.98–7.21, m, 9H, aromatics. The homonuclear ^{1}H (300.133 MHz) 2D-COSY spectrum allows to distinguish between the assigned structure and an alternative one, possibly deriving from III (Y = CH_2CH_2COOH), on the ground that only structure XIII contains a proton which is coupled with other six. Hydrogenation revealed one unsaturation and led to only one of the two possible diastereoisomers. Hydrogenated XIII MS: (*m/e*): 322 (M^+), 298, 281, 249, 231, 215, 205, 191, 173, 167, 157, 143, 117, 105, 91 (base) 83, 69, 59, 55. On ozonation XIII gave a product, the molecular weight of which corresponded to the uptake of two oxygen atoms as expected for PhCO(*o*-C_6H_4)CH_2CH(CH_2CH_2COOMe)CH_2COMe. MS: (*m/e*): 352 (M^+, absent), 296, 295 (base), 277, 263, 221, 217, 208, 207, 195, 194, 178, 165, 115, 105, 91, 77, 59, 43.

XIV (*E*), methyl ester. MS: (*m/e*); 306 (M^+), 291, 274, 259, 246, 232, 219 (base), 217, 205, 191, 178, 165, 155, 128, 115, 91, 77, 59. ^{1}H NMR: δ 1.1, d, 3H, J 6.62 Hz, Me; 2.95–3.12, m, 1H, CH; 3.03, d, 2H, J 5.0 Hz, CH_2; 3.67, s, 3H, OMe; 5.42–5.58, m, 2H, 2=CH; 5.89, d, J 10 Hz, 1H, =CH; 7.14–7.32, m, 10H, 2Ph.

XIV (*Z*), methyl ester. MS: (*m/e*); 306 (M^+), 274, 259, 232, 219 (base), 217, 204, 190, 178, 165, 155, 128, 115, 91, 77, 59. ^{1}H NMR: δ 1.1, d, 3H, J 6.6 Hz, Me; 2.76, d, 2H, J 5.4 Hz, CH_2; 2.95–3.12, m, 1H, CH; 3.63, s, 3H, OMe; 5.42–5.58, m, 2H, 2=CH; 5.92, d, 1H, J 9.8 Hz, =CH; 7.14–7.32, m, 10H, 2Ph.

After hydrogenation XIV (*E*) and XIV (*Z*) gave the same product with saturated chain. MS: (*m/e*): 310 (M^+), 278, 167 (base), 165, 152, 103, 91, 77, 69. ^{1}H NMR: δ 0.91, d, 3H, J 5.7 Hz, Me; 1.33–2.30, m, 9H, 4CH_2, 1CH; 3.66, s, 3H, OMe; 4.02, dd, 1H, J 9.0 Hz, J 6.8 Hz, benzylic CH; 7.25, br s, 10H, 2Ph.

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